ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ACOUSTIC PROPERTIES OF POLYURETHANE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER

M.Sc. THESIS

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Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

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Thesis Advisor: Prof. Dr. Levent Trabzon

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SİLİSYUM OKSİT NANO TOZLARI VE KARBON NANOTÜPLERİ İLE GÜÇLENDİRİLMİŞ POLİÜRETHAN KOMPOZİSYONUNUN AKUSTİK ÖZELLİKLERİ

YÜKSEK LİSANS TEZİ

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Kemal Baran YILDIRIM, a **M.Sc.** student **ITU Graduate School of Science Engineering and Technology of** student ID 513111009, successfully defended the **thesis/dissertation** entitled "**ACOUSTIC PROPERTIES OF POLYURETHANE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER**",which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Jury Members :	**Prof. Dr. Şafak Yılmaz** Istanbul Technical University	
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Date of Submission : 30 September 2015
Date of Defense : 16 October 2015

To my family,

FOREWORD

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Levent TRABZON for his guidance, helpful critics and discussions in my studies.

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October 2015

Kemal Baran YILDIRIM
(Mechanical Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

PU	: Polyurethane
CNTs	: Carbon nanotubes
Iso	: Isocyanate
MWNTs	: Multi-walled carbon nanotubes
S-type	: Spherical type
P-type	: Porous type
PP	: Polypropylene
Rpm	: Revolotions per minute
Wt.	: Weight
CTAB	: Cetyl trimethylammonium bromide
STL	: Sound transmission loss
dB	: Decibels
Absopp. Co.	: Abosrption coefficient
Pbw	: Percent by weight
SAC	: Sound absorption coefficient

LIST OF TABLES

Page

LIST OF FIGURES

Page

ACOUSTIC PROPERTIES OF POLYURETHANE COMPOSITION REINFORCED WITH CARBON NANOTUBES AND SILICON OXIDE NANO-POWDER

SUMMARY

In this study, in order to enhance acoustic properties of polyurethane foam, small amount of carbon-nanotubes and silicon oxide nanopowders were added to the polyol-isocyanate composition. In this thesis, acoustic properties of added small amount of carbon-nanotubes and silicon oxide nanopowders (S-type, P-Type) to the polyurethane composition were determined. By adding CNTs and/or nano-silica in the form of powder or liquid at different concentrations up to 2% within the PU composition to improve the sound absorption were investigated in the frequency range up to 6400 Hz. In this thesis, both CNTs and nano-silica (SiO2) particles were added with different quantities to the isocyante-polyol composition. The properties, especially the sound absorption, were studied for all the prepared samples and results were investigated to come up with the best nanocomposites that can be applied for sound absorption application at the desired operating frequency. For PU nanocomposites, a fixed weight percentage of CNTs (up to 2 wt%) was first mixed with the polyol at 2000 rpm for 10 min using an overhead stirrer equipment. Mixing was started from a speed of about 100 rpm and it was gradually increased to 2,000 rpm for 10 min when the CNT is added to polyol solution. The amount of CNT added was 0.1, 0.35, 0.7, 1.4, and 2 percent of the total weight. Same procedure is applied fot the silicon oxide nano-powder. The small amount of silicon oxide nanopowders (S-type, P-Type) were 0.2, 0.5, 1 percent of the total weight. The isocyanate was added to the polyol mixture having CNTs and/or Nano-silica at diffrent concentrations, and stirred for 10-15 s at 2000 rpm at room temperature before foaming occurred in an open wooden cylindrical mould. The PU foams, which were kept at room temperature for 10 min, were then demolded and cured at room temperature for 1 day.

At the first part of the experiment, sound transmission loss (STL), determined with an impedance tube, was used to characterize our fabricated samples soundproofing properties. The testing was performed according using a Brüel & Kjaer 4206 acoustic test system comprising an impedance tube, speaker, three microphones and a digital frequency analyzer to measure the sound tranmission loss. sound transmission loss measurement of the samples were determined using large impedance tube. Effect of nano-silica and CNTs loading on the sound absorption behavior were investigated and it was concluded that addition of 0.2 wt.% silicon oxide nano-powder and 0.35 wt.% carbon nanotubes to polyurethane composition improved sound transmission loss up to 80 dB than that of pure polyurethane foam sample. More than 40 samples produced having different ratio nano-silica particles and carbon nanotubes were cut into a form having 29 mm diameter for 6400 Hz sound transmission loss measurement. It is concluded that PU with 0.2 wt% of CNTs has better effect than

the rest of the CNTs added samples. It was seen that between 1000-4000 Hz and 5500-6400 Hz the 0.2 wt% of CNTs added PU foam shows better effect on sound tranmission loss. Adding 0.1 wt% of carbon nanotubes has relatively better effect than that of the 1 wt% which leads to a significant increase in absorption ratio at around 4800 Hz.

The system for acoustic measurement consists of a 100 mm tube for a frequency range of 100 – 1600 H and a 29 mm tube for frequencies of 100 - 6400 Hz. For measurement up to 6400 Hz, all produced samples were shaped to be in 29 mm diameter by using hand press tool. It was observed that increasing the amount of the nano-silica content does not increase the sound insulation properties properly. In addition, 1 wt. % of P-type SiO2 content overall has a poor effect comparing the 0.5 wt.% of P-type SiO2. In a large-scale comparison, 0.35 wt. % of CNTs content PU foam has a better sound insulation comparing the pure PU foam and 0.7 wt.% of CNTs added PU foam. In broad frequency range from 100 to 5000 Hz, the sound absorption coefficients of CNTs added PU foams were generally above 0.1, with the maximum of 0.2. It was revealed that there was a significant increase at 6000 Hz where the sound absorption coefficients are maximum 0.5.

Finally, The results of STL and absorption coefficient are presented and compared. As expected, it was found that most of samples are either good in STL or good in absorption. However, some combinations can achieve a balance of performance in both categories.

SİLİSYUM OKSİT NANO TOZLARI VE KARBON NANOTÜPLER İLE GÜÇLENDİRİLMİŞ POLIÜRETHAN KOMPOZİSYONUNUN AKUSTİK ÖZELLİKLERİ

ÖZET

Akustik sönümleme ve ses tranmisyon kaybı özelliğini arttırmak için nano partikül olarak KNT (karbon nanotüp) kullanılması daha önce de araştırılmış ve KNT eklenmesinin ölçülen malzemede akustik absorpsiyonun bütün aralık değerlerinde pozitif yönde katkı sağladığı görülmüştür. Çok düşük oranlarda, örneğin % 0.01 gibi değerlerde dahi KNT eklenmesi görece olarak çok düşük bir etkiye sahip olurken, % 0.1 gibi KNT eklenmesi akustik absorpsiyonun kayda değer bir şekilde % 70'lerden % 90'a yükselmesini sağlamaktadır. Bu tez kapsamında literatürden farklı olarak gözenekli tipte (P-tip) ve küre şeklinde (S-tip) nano-silika tozlarının, karbon nanotüplerin ve bunların karışımının poliüretan kompozisyonuna katılmasının akustik etkisi incelenmiştir. Ses dalgaları iki ana mekanizma ile absorbe edilmektedir; bunlardan bir tanesi mekanik sürtünme, diğeri de direkt termal enerji dağılımına maruz kalmasıdır. Bu tez çalışmasında özellikle silisyum oksit nano tozları ve karbon nanotüpler ile güçlendirilmiş poliüretan kompozisyonunun akustik özellikleri araştırılmış olup kütlece oranı % 2'yi geçmeyecek şekilde farklı oranlara sahip 40'dan fazla numunenin birbirleri ile kıyaslanacak şekilde akustik ölçümleri yapılmıştır. Araştırmanın başında poliüretan oluşumunu sağlayacak izosiyanat ve poliol malzemeleri temin edilmiştir.

Deney aşamasında kullanılan karbon nanotüpler 40 ile 60 µm çapında ve 200 µm uzunuğunda olup 85-90 % saflık değerine sahiptir. Deney sırasında kullanılacak olan karbon naotüplerin etkileşimini arttırmak için hidrojen peroksit (H_2O_2) kullanılarak ultrasonik banoyoya sokulmuştur. İlk aşamalarda 1.5 gram karbon nanotüp 35% H_2O_2'nin 500 ml'si ile ultrasonik banyoya sokulmuştur. Fonksiyonalitesi arttırılan karbon nanotüpler daha sonra oluşan solüsyon hidrojen peroksit'ten arındırılacak şekilde iki kez saf su ile yıkanıp filtreden geçirilmiştir. Bir sonraki aşamada ise 80°C sıcaklıktaki fırında yaklaşık 8 saat tutularak kurutulması sağlanmıştır.

1:1 oranında karıştırılacak izosiyanat ve poliol malzemelerinden, poliol hassas tartı üzerinde tartıldıktan sonra genel ağırlığa göre sırasıyla % 0.35, %,7 ve %2 oranında olacak şekilde karbon nanotüpler karıştırılmıştır. Polilol içerisine konulan karbon nanotüpler ilk önce mekanik karıştırıcı içerisinde yaklaşık 10 dakika boyunca 2000 dakika devir ile karıştırılmaktadır. Böylece poliol ile karbon nanotüplerin iyi bir şekilde karıştırılmış olmaları sağlanır. Daha homojen bir karışım için yüksek hızda değil daha düşük dakika devir değerlerinden başlanarak karışım hızlandırılmıştır. Bir sonraki aşamada artık iyi bir şekilde karışmış poliol ve karbon nanotüp karışımı içerisine izosiyanat dökülmektedir. Hassas terazide kütlece poliol ile 1:1 oranında olacak şekilde ayarlanan izosiyanat, yavaşça poliol-knt karışımı içerisine dökülür. Burada poliol-knt karışımının iki büyük parçadan mamul kalıp içerisine dökülmesi tercih edilir. İzosyinat kalıp içerisinde bulunan karışım içerisine yavaşça dökülür ve

form yapının oluşması için tekrardan mekanik karıştırıcı ile karıştırılır. Poliürethan köpüğün oluşumun hızına bağlı olarak tercihen 10 saniye sürecek şekilde kompozisyon hızlıca 3000 dakika devir hızına getirilerek hızlıca karıştırılır ve köpüğün oluşumu için yaklaşık 1-2 dakika beklenir. Sonuç olarak kütlece arzu edilen karbon nanotüp oranına sahip poliürethan köpüğün oluşumu gerçekleşir. İçerisinde bulunduğu kabın biçimini alacağı için çapı yaklaşık 100 mm, yüksekliği ise 40 mm civarında silindirik bir köpük malzeme üretilmiş olacaktır.

Benzer şekilde, aynı aşamalar nano-silika malzemeler için de gerçekleştirilmiştir. Yüzde bakımında oranları biraz daha farklı olacak şekilde %0.2, %0.5 ve %1 olacak şekilde toz formunda nano-silika malzemeler ilk önce poliol ile karıştırılmıştır. Deneylar sırasında iki farklı tipte silikon oksit nano tozları kullanılmıştır. Bunlardan bir tanesi p-tipli olarak adlandırılmış gözenekli ve 10 µm çapında nano-silika olup bir diğeri s-tipli olarak adlandırılmış küre şeklinde ve bir öncekinden daha büyük çaplı olacak şekilde 15-20 µm çap aralığına sahip nano-silikadır. Her ikisi de toz formunda olup çeşitli kimyasal işlemlerden geçirilmiş ve sıvı formuna getirilmiş nano-silikalar da kullanılmıştır. Özellikle toz formunda nano-silikalar ihtiva eden poliürethan köpük yapısı deney sırasında çok daha dengeli sonuçlar vermiş olup sıvı formundaki nano-silikaların bazı deney sonuçları testin dışında tutulmuştur. Karbon nanotüptekinin benzeri bir şekilde toz formundaki p-tip ve s-tip nano-silika tozlar ilk önce poliol ile karıştırılıp daha sonrasında MDI (izosiyanat) eklenerek karıştırılmaktadır. Burada karışımın ayrı bir kapta karıştırılarak kalıp içerisine dökülebilceği gibi söz konusu kalıp içerisinde karıştırılarak üretilmesi de mümkün olmaktadır. Bir önceki numunelerde de olduğu gibi aynı çap genişliğine sahip olacak şekilde farklı oranlarda köpük malzemeler üretilmiştir. Birbirleri ile etkileşimini daha iyi kıyaslamak için de s tipli ve p-tipli nano tozların bir arada kullanılması gibi, farklı oranlarda karbon nanotüp ve s-tipli/p-tipli nano-silika tozların bir arada kullanılması da araştırılmıştır.

Her bir üretilen numunenin temiz bir sonuç verebilmesi için ses düzeneği içerisine yerleştirilmeye uygun boyutlara sahip olması gerekmektedir. Bunun için kalıp içerisinden çıkarılan her numune daha sonrasında özel torna makinasında şekillendirilmiştir. İlk aşamada kalınlık değerlerinin aynı olması sağlanacak şekilde torna makinası ile 10 mm kalınlığa sahip olacak şekilde ayrlanmıştır. Sonraki aşamada ise 100 mm çapa sahip keskin uçlu basma kalıbı ile her bir numune pres altında kesilmiştir. Böylece, 10 mm kalınlığa ve 100 mm çapa sahip pürüzsüz numuneler elde edilmiştir. Bu şekilde elde edilen 12 adet numune daha sonrasında Brüel & Kjaer 4206 akustik test sistemi içerisinde sırasıyla ölçülmüştür. Ses transmisyon kaybı (sound tranmission loss) ölçülen her bir numune daha sonra birbirleri ile kıyaslanmıştır.

Her bir numune önce akustik test sistemi içerisindeki uygun yere yerleştirilmekte daha sonra sessiz ortamda her bir numunenin ses transmisyon kaybı ölçülmektedir. Oluşturulan grafikler sonucu üretilmiş farklı oranlardaki 30 civarı numunenin birbiri ile kıyaslanması gerçekleşmiştir. Üretim sırasında karşılaşılan ve sonuçlarda da kendisini belli eden bir durum şu şekildedir. Karıştırılan karbon nanotüp miktarı %0.7'i geçmesiyle birlikte poliol ve izosiyanatın birbiri ile etkişelimi kötü yönde olmakta ve yeterli bir şekilde köpük yapının oluşmamasının yanında homojen bir dağılım elde edilememektedir. Elde edilen grafikler yorumlandığı zaman özellikle 100 Hz değerine kadar kütlece % 0.35 ve % 0.7 karbon nanotüpe sahip poliürethan köpük numunesinin daha iyi bir akustik özelliğie sahip olduğu görülmektedir. Diğer

yandan kütlece % 2 karbon nanotüpe sahip poliürethan köpük ise bütün karşılaştırmalarda en kötü sonulardan birine sahip olmaktadır.

Gözenekli tipteki nano-silikalar, yani p-tip nano silikalar %0.2, %0.5 ve %1 oranında olacak şekilde karıştırılmış olup yapılan akustik testler sonucunda en iyi değerlere kütlece %1 karışım oranına sahip nano-silikanın sahip olduğu görülmektedir. Benzer şekilde %0.5 orana sahip nano-silika da büyük oranda aynı grafik eğrisine sahip olmaktadır. Burada bir diğer ilginç konu ise yaklaşık 150 Hz'den sonra saf poliürethanın yani herhangi bir ekleme yapılmamış olan poliürethanın daha iyi bir sonuç vermesidir. P-tip nano-silikalara benzer şekilde s-tip yani küresel tipteki silikalar ile kıyaslanması sonucu %0.2, %0.5 ve %1 oranına sahip numunlerin birbirlerine aynı değerde grafikler elde etikleri görülmektedir. Özellikle 100 Hz'ye kadar % 0.5 s-tip nano-silika oranına sahip numunenin daha iyi akustik sonuç verdiği görülmektedir.

Tez kapsamında ses sönümleme kaybına ilaveten ses absorpsiyon katsayısı da araştırılmıştır. 30'a yakın farklı oranlarda numuneler üretilmiş ayrıca yine nano-silika ve karbon nanotüplerin birbirleri ile farklı oranlarda karıştırılması sağlanarak en iyi akustik özelliklere sahip malzemeye ulaşılmaya çalışılmıştır. %1'e kadar farklı oranlarda karbon nanotüp eklenmiş numuneler içinde yapılmış deneylerde en iyi sonuca %0.2 karbon nanotüp eklenmiş poliüretan numunesinde ulaşılmıştır. Birbirleri ile ypılan kombinasyonlar içerisinde de %0.2 karbon nanotüp ve %1 p-tip nano-silika katılmış numunenin en iyi akustik değere sahip olduğu görülmüştür.

1. INTRODUCTION

In this thesis, acoustic properties of polyurethane compositions reinforced with carbon nanotubes and nano-silica particles were investigated. Both CNTs and nano-silica particles were added with different quantities to the polyurethane foam. By adding CNTs and/or nano-silica in the form of powder at different concentrations up to 2% within the PU composition to improve the sound absorption were investigated in the frequency range up to 6400 Hz. All the prepared samples and results were investigated to come up with the best foams that can be applied for sound absorption application at the desired operating frequency. More than 40 polyurethane foam samples were produced, sound tranmission loss and sound absorption coefficient measuremet of those samples were investigated by using impedance tube to quantify the acoustic characteristics and absorption performance of addition of nanomaterials in comparison with conventional porous materials.

1.1 Purpose of Thesis

Adding small amounts of nanoparticles in a polymer matrix can considerably improve the desired properties of the foam. The properties, especially the sound absorption, were studied for all the prepared samples and results were investigated to come up with the best nanocomposites that can be applied for our sound absorption application at the desired operating frequency. Carbon nanotubes, nano-silica and their mix incorporation on sound absorption of polyurethane foam were investigated. Effects of different parameters such as quantities, mass per unite area and percentage of nanoparticles on PU foams were also investigated. Main purpose of the thesis was that determine the acoustic effects of CNTs and Nano-Silica added polyurethane foams.

1.2 Literature Review

In order to enhance the PU properties, attempts have been made to incorporate appropriate reinforcements into the matrix material [1].

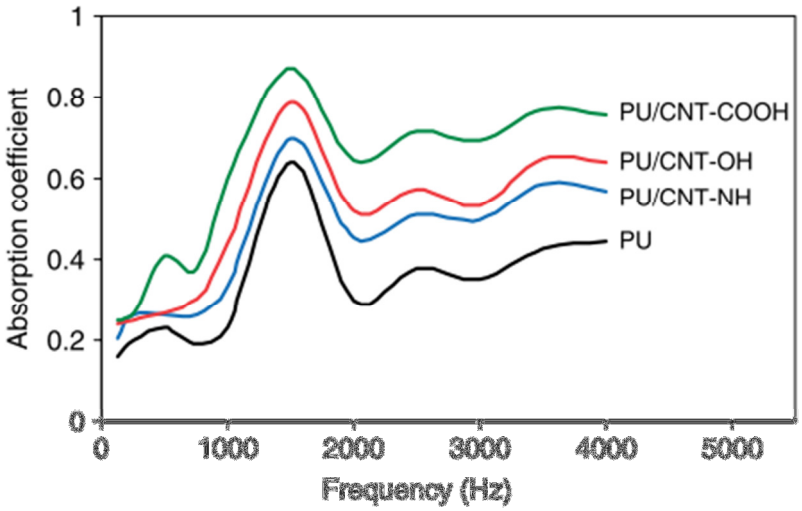


Fig. 1.1 : Absorption coefficient as a function of frequency for neat PU foam and PU nanocomposite foams [1].

Adding small amounts of nanoparticles in a polymer matrix can considerably improve the desired properties of the foam. The nanotubes modified with carboxyl groups were found to have much more influence compared to the other two functional groups, possibly due to better interfacial interaction and improved dispersion [1]. However, the extent of success in enhancing the properties depends strongly on the uniform dispersion of particles at the nanoscale as well as good interaction between the matrix material and nanoparticles. It appears that fibrillar nanoparticles, particularly carbon nanotubes (CNTs), have great potential in the enhancement of PU foam properties. It was shown that by incorporation of only 0.1 wt% CNTs, a significant improvement in acoustic damping can be achieved [2]. SiO2 nanoparticles have also been widely introduced into polymers to improve the heat resistance, radiation resistance, mechanical and electrical properties of polymer materials [3]. However, current studies concerning various aspects of these nanoparticles in PU foams are very limited, and thus further investigations are required.

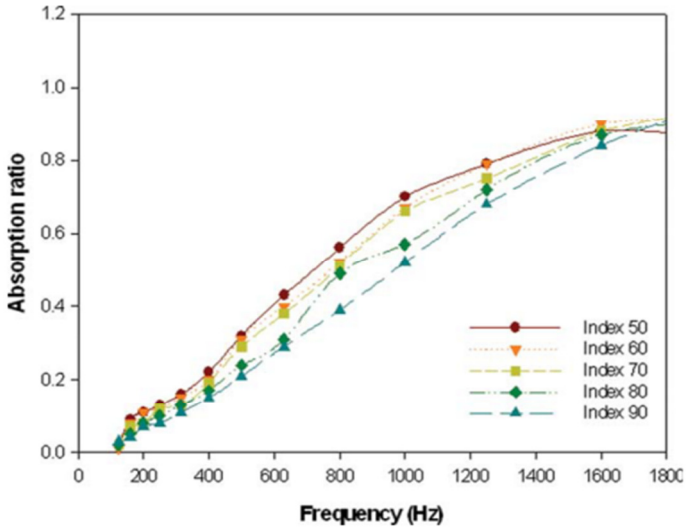


Fig. 1.2 : Sound absorption ratio of PU/nano-silica prepared with different isocyanate index (50–90) [5].

With increasing nano-silica content, the sound absorption ratio of PU/nano-silica foams increases over the entire frequency range investigated. It is believed that presence of small voids is favourable for improving the sound absorption due to the increase in tortuous paths. As the acoustic absorption of PU/CNT-COOH and PU/CNT-OH is higher than that of PU/CNT-NH, it is deduced that the micro-void-dominated mechanism is predominant in improving the acoustic as shown in fig. 1.2 [5].

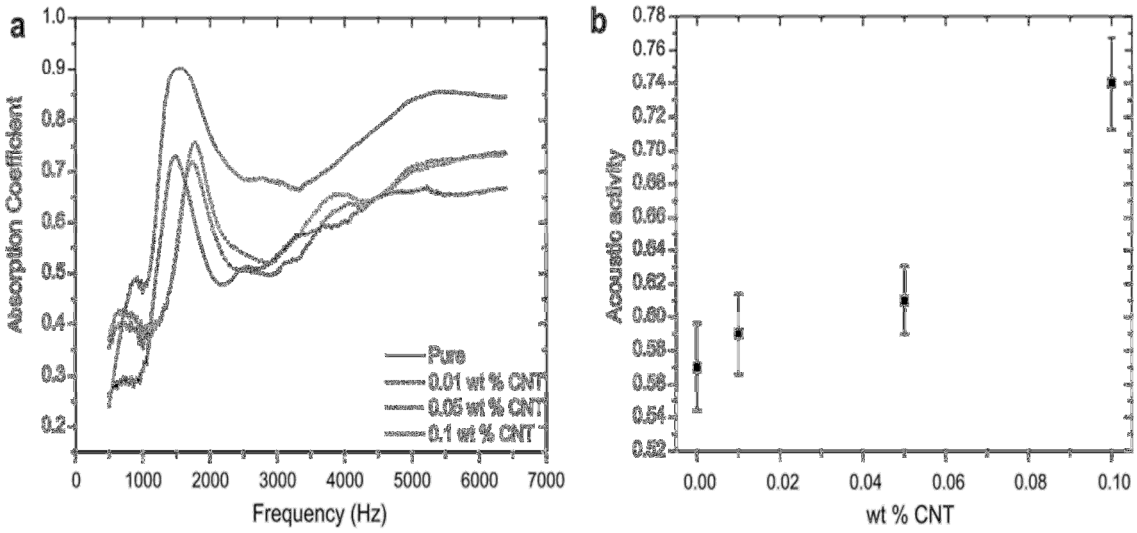


Fig. 1.3 : Acoustic performance of CNT/flexible PU foams. (a) Absorption coefficient as a function of frequency; and (b) acoustic activity of the samples [2].

Flexible polyurethane (PU) foams, with loading fractions of up to 0.2 wt% carbon nanotubes (CNTs), were made by free-rising foaming using water as blowing agent. Electron microscopy revealed an open cellular structure and a homogeneous dispersion of CNTs, although the incorporation of nanofiller affected the foaming process and thus the final foam density and cellular structure. The compressive response of the foams did not show an unambiguous improvement with CNT content due to the variable foam structure [2].

There are also few studies in the literature regarding the use of nanoclay [15], titania nanoparticles [17, 18] multi-walled carbon nanotubes (MWNTs) reinforced polyurethane (PU) for giving rise to considerable improvement in polyurethane foam sound absorption. Especially CNTs having promising mechanical properties were used as a filler to improve sound absorption properties of the PU-based composites [16]. Additionally, nano-silica have been widely introduced into polymers to improve the heat resistance, radiation resistance, mechanical and electrical properties of polymer materials [19, 20]. Nano-silica compositions have remarkable improvement in materials properties. [11]. Nano-silica has the features of small particle size, narrow particle size distribution, porous, large surface area [21].

2. THEORITICAL PART

2.1 Polyurethane

Polyurethane foam, as one of the most common polymer foams, are used in everyday life and applications. Polymer foams are found virtually everywhere in our modern world and are used in a wide variety of applications. It is known that polymer foams have a desirable sound absorption, low thermal conductivity and generally low water absorption. Lots of researches are going on for improving acoustic absorption of the foam.

Polyurethane foams have cellular structure which improves sound absorbing and insulating properties [22]. Mainly two types of PU (polyurethane) foam are used, which are flexible and rigid. Rigid PU foams are generally used for thermal insulation and the flexible ones are used as cushioning transportation and packaging applications. By selecting the reactants and manufacturing process appropriately, PU foam can be made to satisfy a wide range of applications [23]. Polyuretahne can be produced by mixing isocyanate and polyol in predetermined ratio, which then react with each other to form the polymer. Polyurethanes are mostly thermosetting polymers that do not melt when heated. Polyurethane polymers are mostly formed by reacting a di- or polyisocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule. Recently, efforts have been dedicated to minimizing the use of isocyanates to synthesize polyurethanes, because the isocyanates raise toxicity problems.

Polyurethane compositions are used widely overall the world especially for the sound absorption. Due to their cellular structure polyurethane foams have sound absorbing and insulating properties [24].

2.1.1 lsocyanates

Many commercial grades of isocyanates used for making PUs are aromatic in nature. Each isocyanate will give different properties to the end product, requiring different curing systems and, in most cases, different processing systems. An important

property of an isocyanate is its functionality, i.e. the number of isocyanate groups (-NCO) per molecule. For cross linked PU applications the average functionality of the isocyanate is usually a little over two. The higher functionality isocyanates are used for special applications. When a di-functional isocyanate is used with a di-functional polyol a long linear PU molecule for elastomeric applications is formed. The common isocyanates used to make PU foams are shown in figure 2.1 [12].

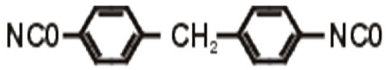


Figure 2.1 : MDI (diphenylmethane 4,4 - diisocyante) chemical formula

A fundamental feature of isocyanates is their high reactivity. The reaction of the isocyanate groups with one another or with small NCO-reactive molecules (for example water or short-chain mono- or polyhydric alcohols) is utilized in the modification reaction for the preparation of polyisocyanates, the crosslinking agents for coatings [14].

On the other hand, figure 2.2 shows examples of some common isocyanates [26].

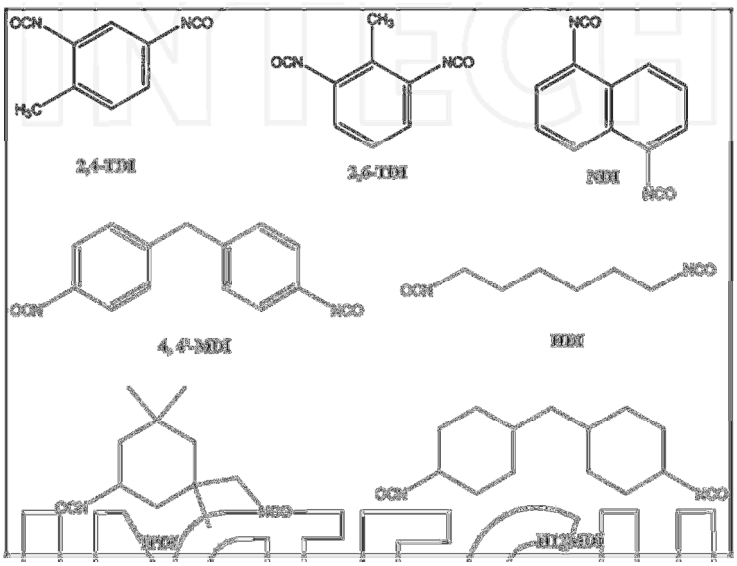


Fig 2.2 : Common isocyanates.

Required properties for PU foam can be arranged by selecting different type of isocyante. For eample, to prepare rigid PU foam, aromatic isocyanates can be chosen.

2.1.2 Polyols

A polyol is an alcohol containing multiple hydroxyl groups. In two technological disciplines the term "polyol" has a special meaning: food science and polymer chemistry. Polyol is is the second primary component of a polyurethane formulation. The name polyol refers to chemical compounds containing multiple hydroxyl groups. Polyols are used in both food science and polymer chemistry, including the formulation of polyurethanes. In polymer chemistry polyols are polymers or monomers with hydroxyl functional groups available for organic reactions The primary application for polyols is the manufacture of flexible or rigid polyurethane foams.

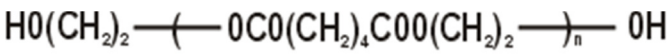


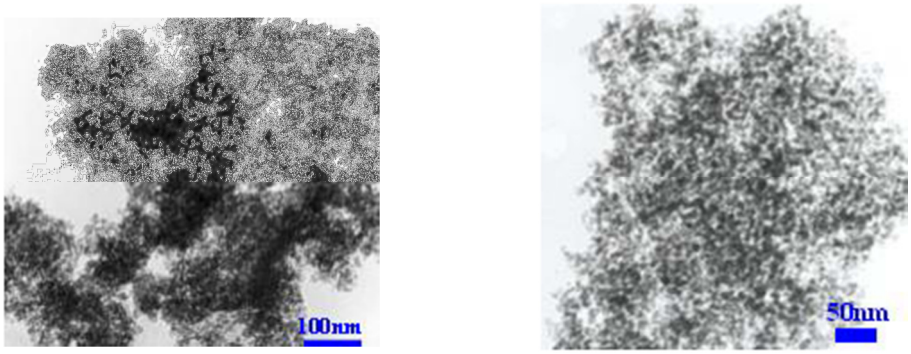
Figure 2.3 : Polyethylene adipate (a polyster) chemical formula.

Polyol blend remains unchanged until it is reacted with an isocyanate to form a polyurethane. There are two main types of polyols used in the PU industry, polyethers and polyesters. PU foam was prepared by mixing the polyol and isocyanate at a 1:1 ratio. The amount of water coming into the formulation as residual in the polyol can be calculated and used to adjust the amount of water to be purposely added.

2.1.3 SiO2 Nano-Particles

Silicon dioxide nanoparticles, also known as silica nanoparticles or nano-silica, are the basis for a great deal of biomedical research due to their stability, low toxicity and ability to be functionalized with a range of molecules and polymers [29].Nano-silica particles are divided into P-type and S-type according to their structure. The P-type particles are characterized by numerous nanopores having a pore rate of 0.61 ml/g. The S-type particles have a comparatively smaller surface area. The P-type nano-silica particles exhibit a higher ultraviolet reflectivity when compared to the S-type. Silicon belongs to Block P, Period 3 while oxygen belongs to Block P, Period 2 of the periodic table.

Nano-silica particles according to their structure, as mentioned above, are divided into two types: P-type (Porous particles) and S-type (Spherical particles). During the all related experiments, P-type (Porous particles) and S-type (Spherical particles) were used. P-type nano-silica surface contains a number of nano-porous with the pore rate of 0.611ml /g; therefore, P-type has much larger SSA comparing to S-type (See US3436). US3440 is P-type and its SSA is ~640m2/g. Furthermore, P-type ultraviolet reflectivity is >85%,



(a) **(b)**

Figure 2.4 : Image of (a) P-type nano-silica at 100 µm
(b) S-type nano-silica at 50µm

There is a wide range of product application in different fields with a large different amount of dosage, from 0.5 to 5.5%. Nano-silica particles according to their structure are divided into two types: P-type (Porous particles) and S-type (Spherical particles). P-type nano-silica surface contains a number of nano-porous with the pore rate of 0.611ml /g; therefore, P-type has much larger SSA comparing to S-type Furthermore, P-type ultraviolet reflectivity is >85% , S-type: >75%. Paint, plastic, color rubber, magnetic materials, in addition, nano-silica can be widely used in ceramics (sugar) porcelain, gypsum, batteries, paints, adhesives, cosmetics, glass, steel.

2.2 Basic Polyurethane Chemistry

The simplest PU is linear in which the hydroxyl compound and the nitrogen compound each have a functionality of two. This can be represented by the following:

Isocyanate + Polyol = Polyurethane

The isocyanate can react with different chemical groups, so the final properties of the polymer will vary according to the reaction route taken. Therefore the formulation of a PU must take into account every possible reactive constituent. PUs may have a very widely varying structure depending on the type of isocyanate and the type of reactive hydrogen components present in the formulation. The presence or otherwise of the various groups along the urethane linkage will control the end properties of the polymer. The curing of a PU can be regarded as the formation of a network, also called crosslinking, the extent or degree of cure is often expressed as the crosslink density [12].

Polyurethanes are the reaction product of an isocyanate and a hydroxyl group. Poly indicates that more than one urethane group is involved. Typically diols or polyols (di is "two" functional and poly is more than 2) and a diisocyanate or polyisocyanate is used to prepare a polyurethane. A hydroxyl group is a reactive group which consist of one hydrogen and oxygen.

The reactivity of the isocyanate group can be explained by considering the resonance possibilities presented in the figure below.

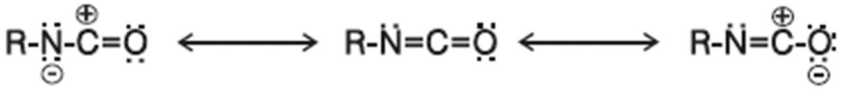


Fig. 2.5 : The reactivity of the isocyanate group.

Electron density is expected to be greatest on the oxygen atom and least on the carbon atom. This results in the oxygen atom having the largest net negative charge, the carbon a net positive charge, and the nitrogen, an intermediate net negative charge.

2.3 Sound Absorption

Sound is a mechanical wave that is an oscillation of pressure transmitted through a solid, liquid, or gas, composed of frequencies within the range of hearing. Sound waves are often simplified to a description in terms of sinusoidal plane waves, which are characterized by these generic properties. Acoustic absorption is that property of any material that changes the acoustic energy of sound waves into another form, often heat, which it to some extent retains, as opposed to that sound energy that material reflects or conducts. Acoustic absorption is represented by the symbol A in

calculations. Absorption is not a single mechanism of sound attenuation: propagation through a heterogeneous system is affected by scattering as well.

Materials have acoustical properties such as absorption, reflection or transmittance. Acoustical materials are those materials designed and used for the purpose of absorbing sound that might otherwise be reflected. Sound absorption is defined, as the incident sound that strikes a material that is not reflected back. An open window is an excellent absorber since the sounds passing through the open window are not reflected back but makes a poor sound barrier. Painted concrete block is a good sound barrier but will reflect about 97% if the incident sound striking it [27].

When a sound wave strikes an acoustical material the sound wave causes the fibers or particle makeup of the absorbing material to vibrate. This vibration causes tiny amounts of heat due to the friction and thus sound absorption is accomplished by way of energy to heat conversion.

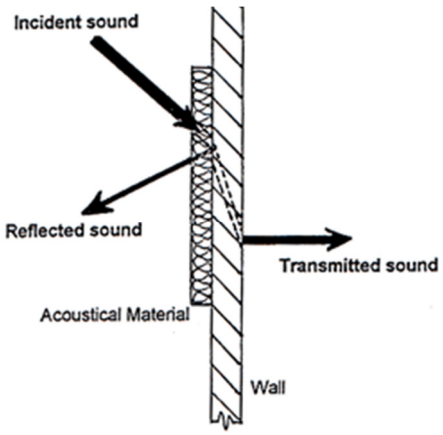


Fig. 2.6 : An image of a sound wave absorption

As sound travels though any medium, as shown in fig. 2.5, there is some loss due to absorption. Since sound is a regular vibration of the atoms or molecules in a material, some of the kinetic energy of the waveform is lost due to molecular collisions. That sound energy is turned into random heat energy. Some materials absorb sound more than others. Drapes and ceiling tiles are used to absorb unwanted sound and eliminate echoes. When a wave reaches the boundary between one medium another medium, a portion of the wave undergoes reflection and a portion of the wave undergoes transmission across the boundary.

2.3.1 Sound Transmission Loss

Sound transmission loss (STL) is the number of sound decibels that are stopped by a wall or other structure at a given frequency. In the graph below, the green line represents the transmission loss of a wall at different frequencies. A measure of the sound-insulation value of a partition; the amount, in decibels, by which the intensity of sound is reduced in transmission through the partition.

Measurement of transmission loss can be in terms of decibels. Mathematically, transmission loss is measured in dB scale and in general it can be defined using the following formula:

$$TL = 10\log_{10}\left|\frac{W_i}{W_t}\right|$$

where:
W_i is the power of incident wave coming towards a defined area (or structure); W_t is the power of transmitted wave going away from the defined area (or structure) [28].

Sound Transmission Loss (STL) is tested using a two chamber technique. One chamber houses a sound emitter. The other chamber houses a sound receiver. The two chambers are separated by the product being tested.

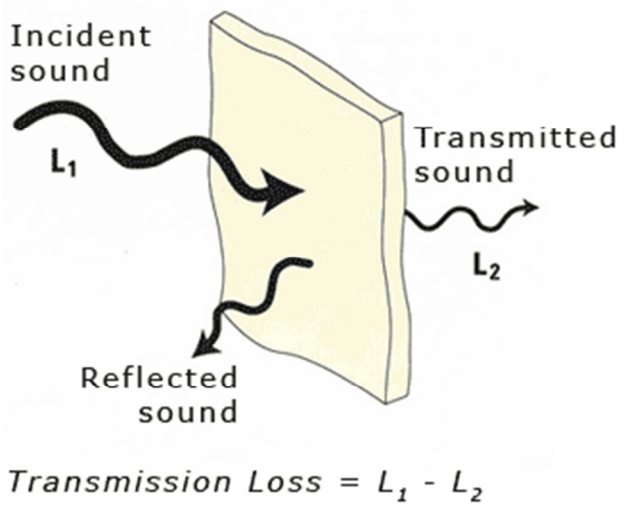


Fig. 2.7 : A sound barrier showing transmission loss.

Sounds at specific frequencies and intensities are produced by the emitter. The sound intensity transmitted through the glazing barrier is measured at the receiver. The difference in intensity between the sound source and the sound reception is the Sound Transmission Loss at that frequency. STL tests are normally carried out at eighteen standard frequencies at 1/3 octave frequency bands between 100Hz to 6400Hz. The results of a STL test are used to quantify acoustic performance against common indices.

2.3.2 Sound Absorption Coefficient

The absorbing coefficient can be mathematically presented as follows:

$$\alpha = 1 - \frac{I_R}{I_I}$$

where α, I_R , and I_I are the sound absorption coefficient, one-sided intensity of the reflected sound and the one-sided intensity of the incident sound, respectively. from the above equation, it can be observed that the absorption coefficient of materials varies from 0 to 1. there are several standard methods to measure sound absorption coefficient. In one of the common approaches,a plane wave impedance tube that is equipped with two microphones is utilized.

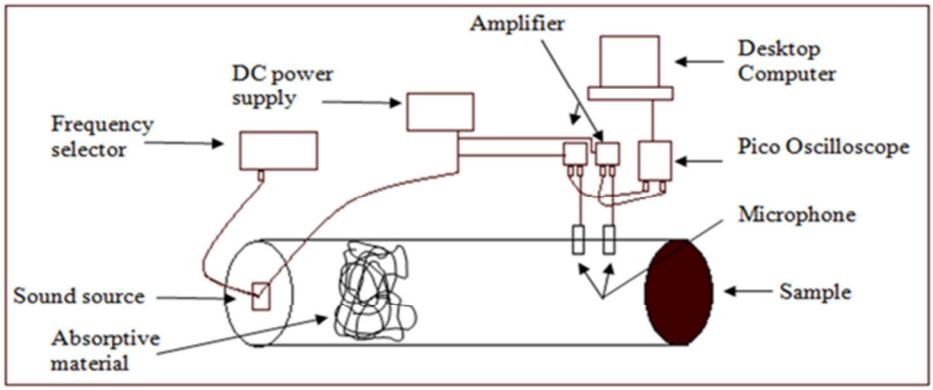


Fig. 2.8 : Schematic diagram of sound absorption coefficient measuring system.

Figure 2.7 show a schematic diagram of Sound absorption coefficient measuring system. The reflector of a surface on material can be used to determine the

absorption coefficient of a surface. The absorption coefficient of a surface is a very useful parameter as it states the fraction of that energy that is absorbed when sound is incident to a surface.

3. EXPERIMENTAL PART

Polymer foams are a group of lightweight materials, which are made up of a gaseous phase distributed uniformly within a polymeric matrix. Polyurethane (PU) foams are known to be the most widely used plastic foams. They are important and versatile materials due to their outstanding strength-to-weight ratio, their resilience, and their electrical, thermal, and acoustic insulating properties, amongst other characteristics. This type of plastic foam is produced via the polymerization reaction of a diisocyanate with a polyol in the presence of water as blowing agent. The polymerization reaction and foam blowing occur simultaneously during PU foam production. The polymer structure must build up rapidly to support the fragile foam, i.e. to form a stable cellular structure, but not so fast as to stop bubble growth. In order to control the reaction rate as well as the cell structure, suitable surfactant and catalyst are needed to add into the reaction mixture.

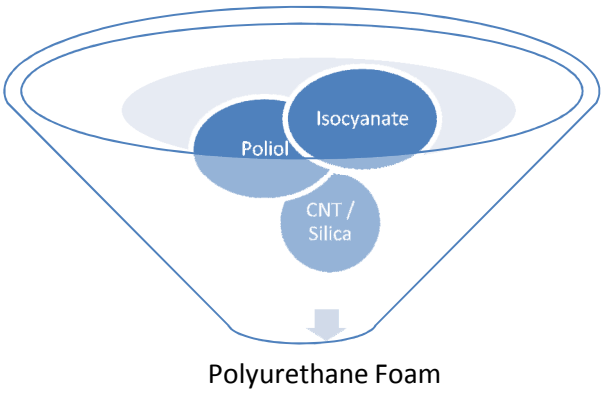


Fig 3.1 : Basic schematic of the polyurethane.

The appropriate surface modification on nanoparticles, not only leads to better dispersion and compatibility of nanoparticles in polymer matrix, but also can form chemical and physical interactions with polymer matrix, which guarantee a durable chemical junction between the two incompatible phases. [3]. Recipes for obtaining PU with CNT and nano-silica particles can be modified to include some additives that might improve the properties of the foam.

3.1 SiO2 Nano-Particles Preparation

SiO2 nano-particles used in this experiment has two different diameters, shown in table 3.1, of about 15-20 nm and 10 nm. At first, 1 g of blank or surface treated nano-silica was dispersed into 10 ml acetone solution with 30 min ultrasonation, respectively. Then, 20 g of PPG was put in to get a mixture suspension. Afterward, the mixture suspension was kept at 80°C for 4 hours with stirring; hence surface treated PPG/SiO2 dispersions were obtained. Even the PPG/SiO2 dispersions were obtained, powder form of the Nano-silica was also used in the experiments. Silicon dioxide nanoparticles, also known as silica nanoparticles or nanosilica, are the basis for a great deal of biomedical research due to their stability, low toxicity and ability to be functionalized with a range of molecules and polymers [25]. As mentioned before, Nano-silica particles according to their structure are mainly divided into two types: P-type (Porous particles) and S-type (Spherical particles). P-type nano-silica surface contains a number of nano-porous with the pore rate of 0.611ml /g;. In our experiment, these two different type of nano-silicas were used (table 3.1). One of them is Silicon Oxide Nanopowder (SiO2, 99.5+%, S-type (Spherical), 15-20 nm, amorphous) and the other one is Silicon Oxide Hollow Micron Powder (SiO2, 99%, P-type (Porous), 10um, amorphous).

Table 3.1 : Properties of Silicon Oxide Nanopowder.

Materials	Characteristics
Silicon Oxide Nanopowder (S-Type)	(SiO2, 99.5+%, S-type (Spherical), 15-20 nm, amorphous)
Silicon Oxide Hollow Micron Powder (P-Type)	(SiO2, 99%, P-type (Porous), 10um, amorphous)

Prior to the synthesis of PU nanocomposite foams, nano-silica was first mixed with PPG for 2 hours using a high speed mixer (with sonication). Subsequently, the surfactant, catalyst, crosslinking agent and distilled water were added if necessary to the PPG/nano-silica mixture and mixed at 5200 rpm for 5 min.

3.1.1 Preperation of carbon nanotubes

The diameters of CNTs used in the experiment are vary from 40 to 60 nm with a length of around 200 μm and purity %85-90. CNTs were first chemically-treated with a 3:1 concentrated sulphuric–nitric acid mixture followed by three times filtering and washing with distilled water [10]. A surfactant, catalyst and distilled water, percentage by weight of the reactants shown in table 3.4, is suggested to be added to the CNT/polyol mixture, and mixed at 2000 rpm for 1 min using the stirrer until the mixture becomes a homogeneous phase.

Tablo 3.2 : Percentage by weight of the reactants.

	% Weight
Polyol	43.7
MDI	53.2
Water	1.7
Catalyst	0.9
Surfactant	0.5

The CNTs was functionalized by treating with the hydrogen peroxide (H2O2). A 1.5 g sample of CNTs were sonicated with 500 mL of 35% H2O2 at room temperature for 90 min. The solution was then filtered and washed twice with DI water to remove any H2O2 and dried in the oven at 80°C for 8 hours.

3.2 Preperation of PU Foam For Sound Transmission Loss Mesaurement

As mentioned before, isocyanate and polyol were used to produce the polyurethane. Properties of polyol and isocyanate used in the experiments are shown in the table 3.2. Nanoparticles tend to aggregate and show very poor dispersion in polymers, the aggregation is more and more serious with the particle size reduced. To achieve good dispersion of nanoparticles and yield better compatibility between nanoparticles and polymer matrix, CNTs was functionalized by treating with the hydrogen peroxide.

Table 3.3 : Properties of H 1710/06 polyol and isocyanate components.

Physical properties	Unit	Polyol	Isocyanate	Standards
Density (20°C)	g/cm3	1.1	1.230	DIN 51 757
Viscosity (20°C)	Mpa.a	-	210	DIN 53 018
NCO content	H2O	-	31,5	ASTM D 5155-96 A
Storage life	Month		6	

Both CNTs and nano-silica particles were added with different quantities to the polyurethane foam. By adding CNTs and/or nano-silica in the form of powder and liquid at different concentrations up to 2% within the PU composition to improve the sound absorption were investigated

H 1710/06 polyols were used in our experiments, which is shown in figure 3.2.

Fig 3.2 : H 1710/06 Polyol used for the production of PU foam.

Prior to the synthesis of polyurethane foams, different weight ratios such as 0.1, 0.2, 0.35, 0.7, 2 wt.% of CNTs were mixed with H 1710/6 polyol (table 3.2) at 2000 rpm for 10 min by using a mechanical stirrer equipped with a stirrer tip. The stirrer tip made from polymer material for preventing any kind of reaction with the composition. Table 3.3 shows the percentage of the nanoparticles as additives of the samples used for producing PU foams.

Fig. 3.3 : A picture of isocyanate used for production of the PU Foam.

After added polyol was calculated, predetermined amount of the CNTs were added to the polyol for mixing. What we observed is that increasing amount of the CNTs cause to decreasing homogeneity of the PU composition.

(a) **(b)**

Fig. 3.4 : (a) A picture of CNTs in a plastic bottle taken during the experiment.
(b) A picture of a measured polyol in a case.

3.2.1 Preparation of carbon nanotubes added pu foam

For the PU foam, a fixed weight percentage of CNTs (up to 2 wt%) was first mixed with the polyol at 2000 rpm about 10 minutes by using an overhead stirrer equipment, as shown in Fig. 3.5.

No surfactant, catalyst nor distilled water was added to the CNT/polyol mixture at this stage. When the PU sample was synthesized at high speed, the CNT additives do not disperse homogeneously. Therefore, the mixing was started from a speed of about 100 rpm and it was gradually increased to 2,000 rpm for 10 min when the CNT was added to polyol solution. The amount of CNTs content was 0.1, 0.2, 0.35, 0.7, and 2 percent of the total weight.

Figure 3.5 : Overhead stirrer used for mixing the composites.

Next step, said mixture was poured into a cylindrical wooden mould and the isocyanate was added and stirred for 10-15 s at 2000 rpm [4] at room temperature. When the PU sample was synthesized, as shown in Fig. 3.6, the foams, which were kept at room temperature for 10 min, were then demolded and cured at room temperature for 1 day before characterization.

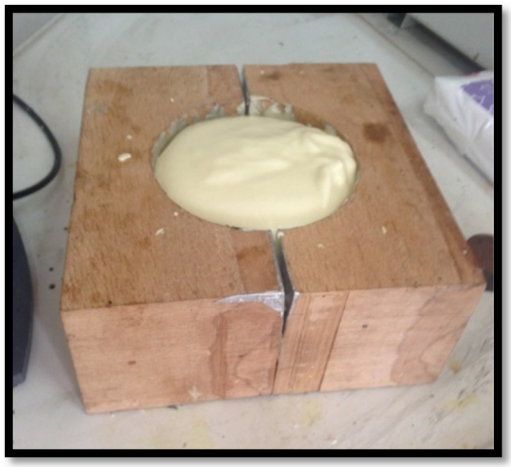
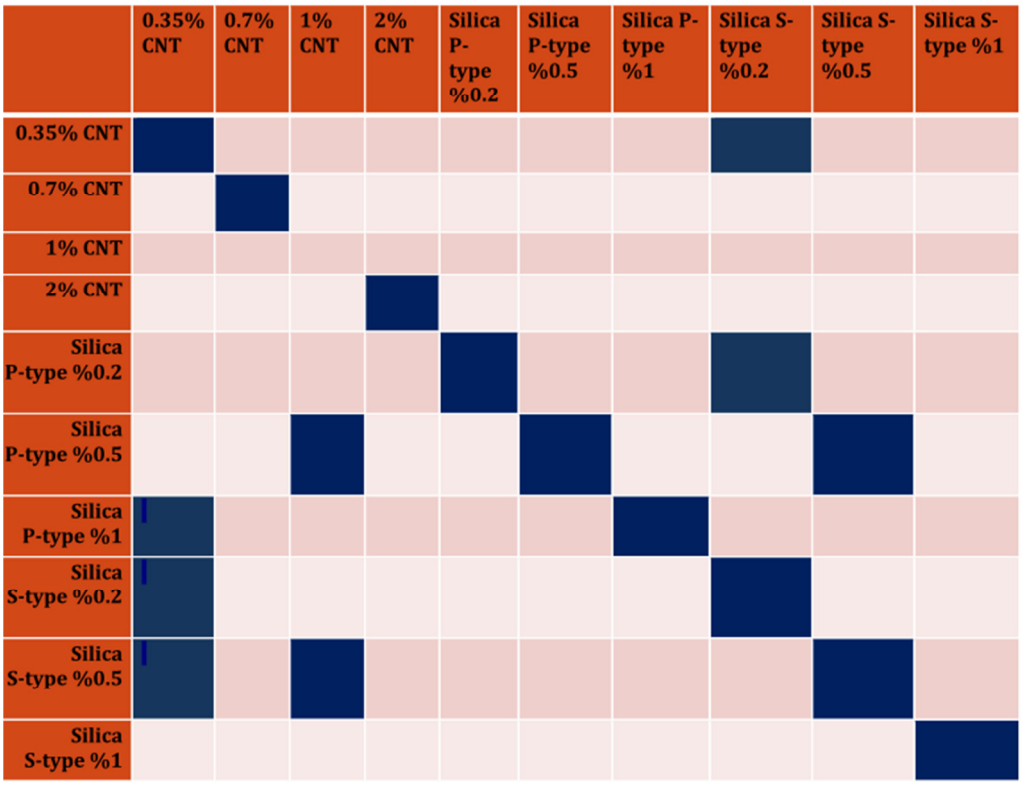


Figure 3.6 : The wooden mould used for PU foam preparation.

Table 3.4 : Percentage of the additives of the PU foam samples mixtures.



Same procedures were repeated according to the different weight ratios of nanp-silica, CNTs and combination of Nano-silica and CNTs. The PU foams were prepared by mixing CNTs and/or Nano-silica with the polyurethane matrix. At the beginning of the experiments, it was necessary to define different weight ratios of CNTs and Nano-silica in the PU foam. For determining the best PU foam having better acoustic properties, many samples having different CNTs and/or nano-silica weight ratios were produced. The range of weight ratio of nanoparticles varies between zero to two.

Table 3.3 shows the percentage of the additives of the PU foam samples mixture. The PU foams were prepared at different weight ratios of nano-silica, CNTs, their combinations such as: ((Nano-silica P-type (0.5 wt%) + CNTs (1 wt%)), (Nano-silica S-type (0.5 wt%) + CNTs (1 wt%)) and (Nano-silica P-type (0.5 wt%) + Nano-silica S-type (0.5 wt%)). At least 30 different types of reinforced PU foams were produced.

3.3 Shaping the Samples For Acoustic Measurement

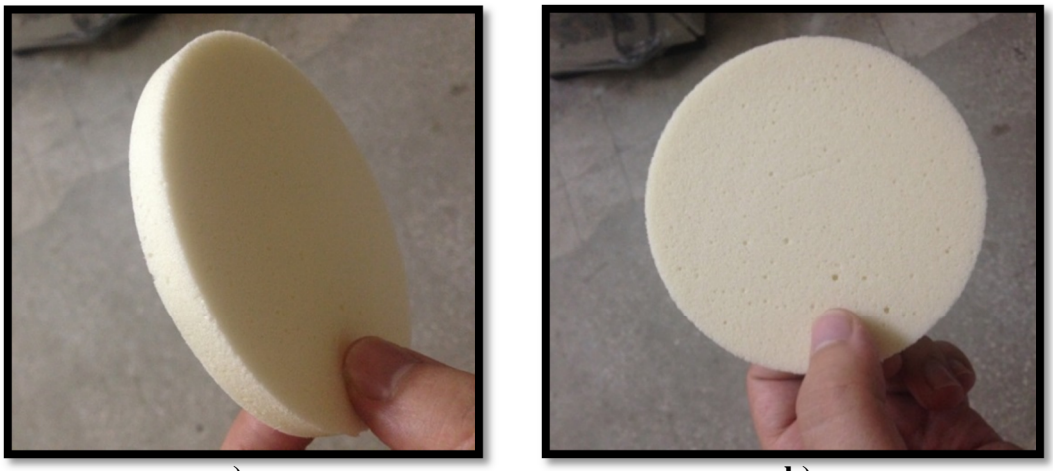
The wooden die consisting of two-piece wooden part was manufactured for forming of the PU foam to prepare samples for acoustic measurements. Every produced PU sample were cut for getting a perfect cylindrical shape in a size 100 mm X 100 mm X 10 mm. Every sample of formed PU foams was placed in a proper area in the lathe, shown in fig. 3.7, and rotated about a horizontal axis against a tool for shaping it in a desired size

Fig. 3.7 : Lathe machine used for shaping the PU samples.

The thickness of the every PU foam sample was arranged to be in 1 cm. Immediately afterwards, sliced PU foam were placed on a plate and a metal cylindrical piece having an open end in an exact 100 mm diameter (shown in figure 3.8) with a sharp-edges were pressed against the sample under a hand press (figure 3.8). As the hand press process were done, the sample was 100 mm in diameter. After all processes were done, all samples were in a shape having 1 cm thickness and 100 mm in diameter**.**

Fig. 3.8 : Pressing tool for shaping the samples to be in a form having 100mm diameter in each sample.

As mentioned before, every sample was shaped and sliced to be in a perfect desired size for acousticg tests. It was very important that every sample was in a same shape for consistency. An example of the PU foam sample, which was cut and sliced, is shown in Fig. 3.9 (a) and (b).



a) **b)**

Fig. 3.9 : a) A figure of a PU sample after 10 mm slicing and 100 mm cutting process. **b)** Another view of the sliced PU sample.

As it is shown above, the PU foam samples were cut and sliced to be in a form cylinder having 100 mm in diameter and 10 mm in thickness. Porous forms on the surfaces also can be seen on top and bottom faces of the PU sample. More than 40 samples have been produced and shaped as mentioned above for determine acoustic properties. For decent measurement, one of the most important points was that shaping of the PU form. It is clear that all the samples should have the same diameter and thickness for a decent comparison.

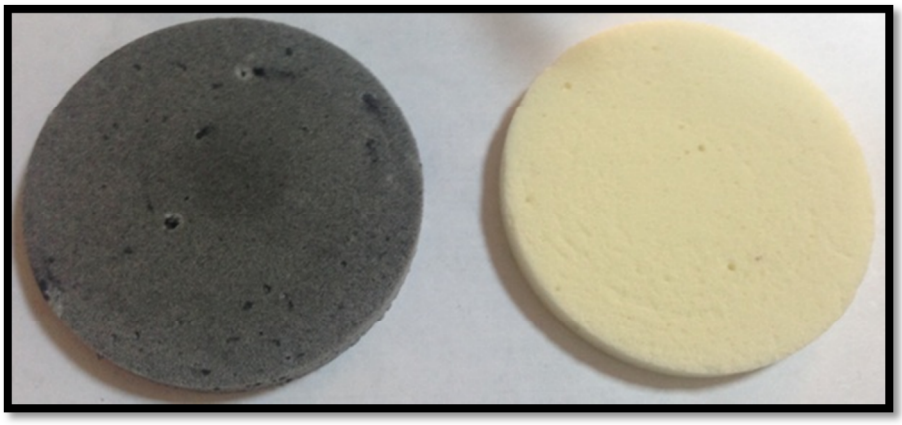


Fig. 3.10 : A photograph of a PU sample / CNTs (left) added and Nano-silica (right) added.

Referring to the CNTs added PU foam, upper surface of the CNTs added PU foam has more bubbles on its surface than the Nano-silica added composition. What we observed during the production is that increasing the amount of the carbon nanotubes prevents better interaction of the polyol and isocyanate with each other.

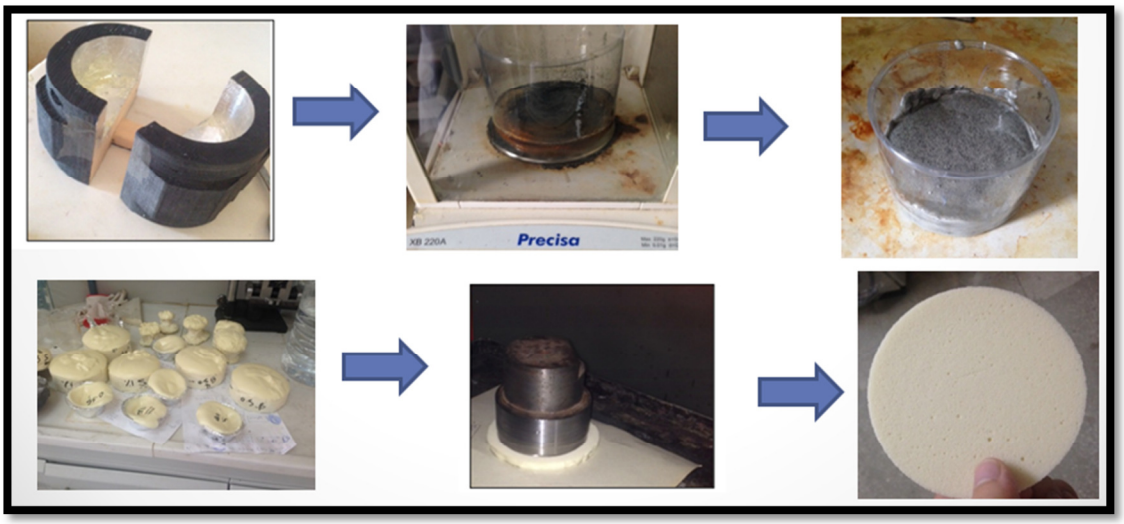


Fig. 3.11 : Basic schematic of the PU foam production and shaping.

Fig .3.11 shows a basic schematic of the PU foam production and shaping, fig. 3.12 shows a hand press tool was used by a metal piece having an open end and exact 29.5mm diameter. Previously produced samples were respectively cut by using said hand press tool.

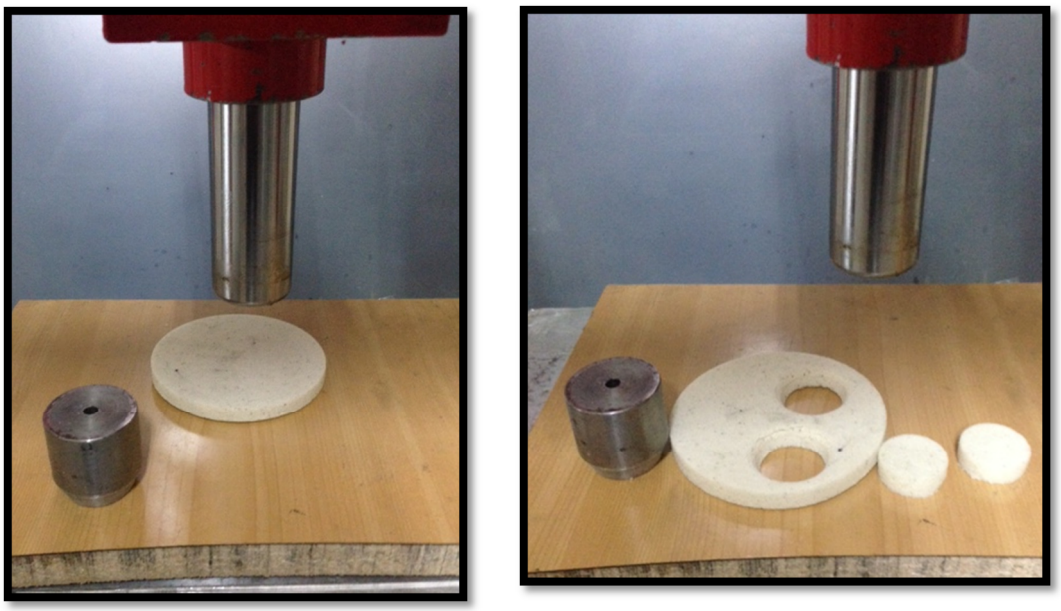


Fig. 3.12 : Hand press for shaping to diameter 29 mm.

The small and large tube setups of impedance tube were used to measure different acoustical parameters and then large and small tube measurements were combined to determine the sound absorption rate for the frequency range of 50 - 6300 Hz. Referring to fig. 3.12, samples having 29 mm diameter were cut to fit in small tube for acoustical measurement.

4. RESULTS AND DISCUSSIONS

4.1 Sound Transmission Loss Measurements up to 1600 Hz

STL, also known as the sound reduction index, is the ability of a material to isolate a sound. The sound TL characteristics of building construction are recognized as one aspect of the total design criteria. At first step sound transmission loss (STL), determined with an impedance tube [6], was used to acoustic characterize our fabricated samples soundproofing properties. The testing was performed according using a Brüel & Kjaer 4206 acoustic test system, shown in Figure 4.1, is comprising of an impedance tube, speaker, three microphones and a digital frequency analyzer to measure the sound transmission loss. Sound Transmission Loss (STL) represents the amount of sound, in decibels (dB), which is isolated by a material or partition in a particular octave. At first step STL was determined, at the other part of the experiments, absorption coefficient of the CNTs and/or nano-silica added PU foams were determined.

Fig. 4.1 : Brüel & Kjaer 4206 acoustic test system.

The sound absorption measurements were performed according to ISO 10534-2 and ASTM E1050-98 international standards for horizontally mounted orientation-sensitive materials using a two-microphone transfer-function method. The sound transmission loss is defined as the ratio of the acoustic energy absorbed by the foam to the acoustic energy incident (incident) on the surface and is dependent on frequency over the frequency range from 0 to 1600 Hz. In the first phase of the work, different materials were examined for their sound transmission loss in a normal wave impedance tube in the frequency range 0-1600 Hz. The small and large tube setups were used to measure different acoustical parameters and then large and small tube measurements were combined to determine the sound absorption coefficient for the frequency range of 50–6300 Hz.

At the first part of the experiments, the PU samples with 0.1%, 0.35%, 0.70%, 1.4% and 2.0% of CNTs, and 0.2, 0.5 and 1% of both small (P-type) and large size (S-type) silica nano-particle as well as the mixture of CNTs and both small and large nanosilica (1 + 0.5%) each and a mixture of small and large nanosilica (0.5 + 0.5%) were tested at the frequency ranging from 0 to 1600 Hz. The sound transmission loss of the samples was measured, as mentioned above, having 100 mm in diameter and 10 mm thick.

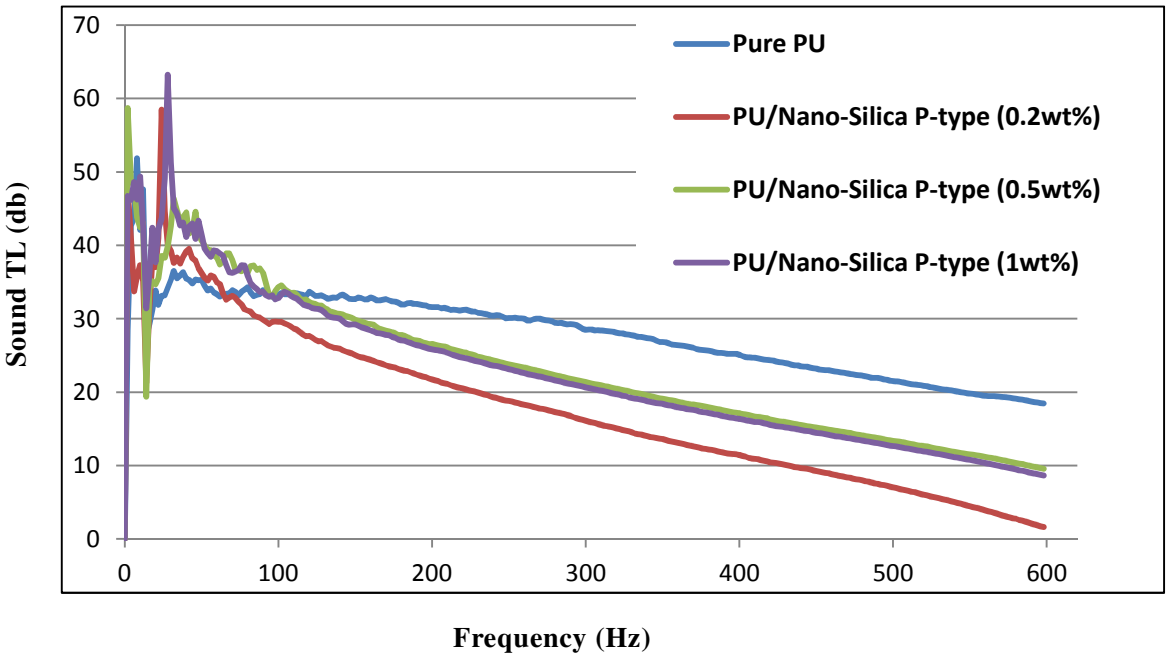


Fig. 4.2 : Sound tranmission loss of PU/ large nano-silica composites.

Figure 4.2 shows that, up to 100 Hz, increasing the amount of large nano-silica shows a better sound absorption properties. After about 120 to 600 Hz, the pure PU shows better effect on sound tranmission loss. Adding 0.2 and 0.5 wt% of nano-silica has relatively better effect than that of the 1 wt% which leads to a significant increase in absorption ratio at around 50 Hz. Almost similar results were obtained in large nano-silica (S-type) PU foams (fig. 4.3).

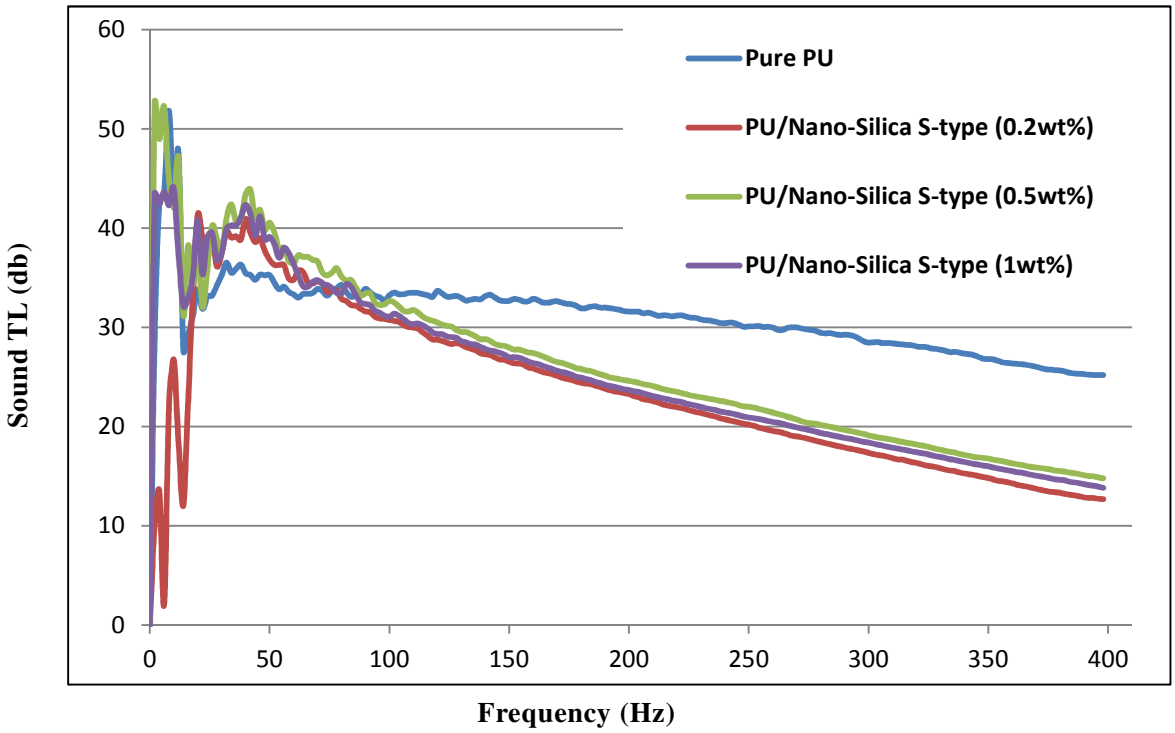


Fig. 4.3 : Sound tranmission loss of nano-silica S-type added to PU foam.

Fig. 4.3 shows that, up to 100 Hz, increasing the amount of large nano-silica PU composite has a better sound absorption. PU foam with 0.5% and 1% weight concentration of nano-silica has relatively better effect than that of the 0.2 wt%. Results obtained from s-type nano-silica PU foam up to 400 Hz. have the almost same correlation with p-type nano-silica as shown in fig. 4.2.

Addition of small amount of nano-silica in the powder form to a polyurethane matrix does not change sound absorption characteristics significantly compared to pure PU up to 400 Hz. In addition, increasing the nano-silica content to %1 does not make a noticeable change in the acustic characteristics.

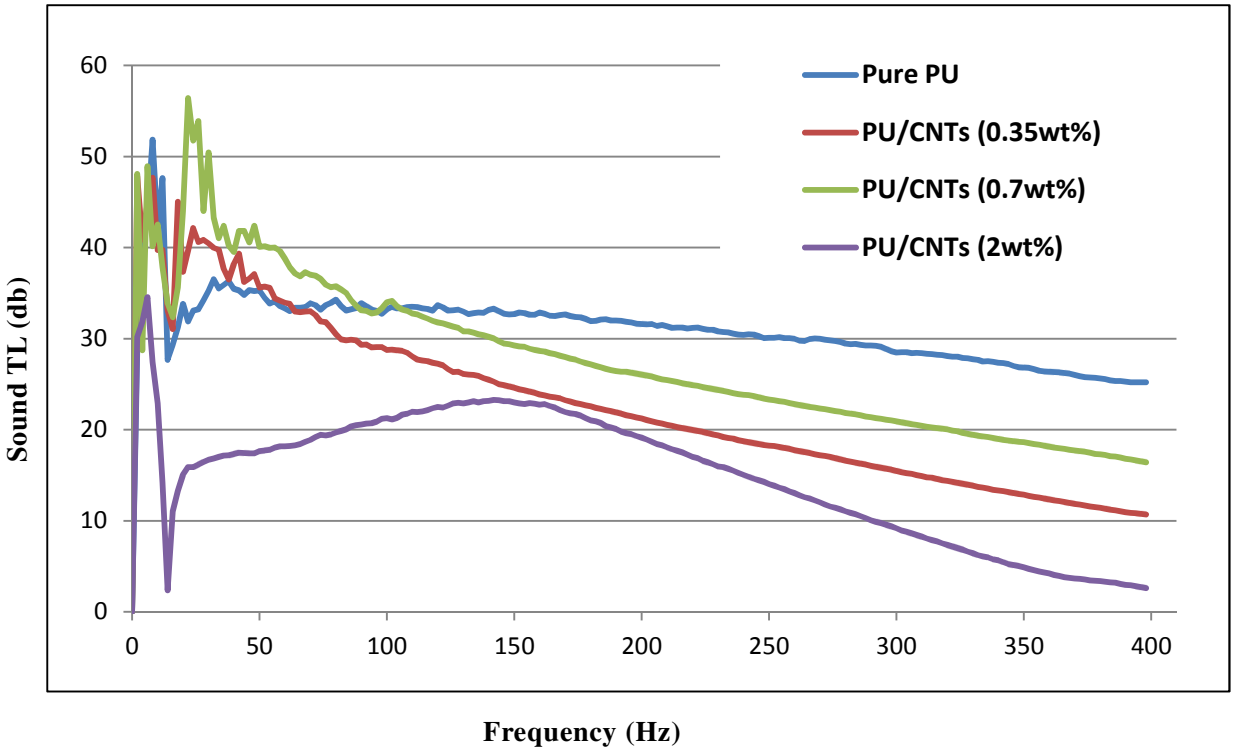


Fig. 4.4 : Sound tranmission loss of CNTs added PU Foams.

Referring to the fig 4.4, 0.35 wt% and 0.7 wt% of CNTs content have a better sound insulation compared to the pure PU foam between 30-70 db. Surprisingly, addition 2 wt% of CNTs has a poor effect compared to the pure PU foam. One the reason is that, increasing the amount of CNTs cause the prevent interaction of polyol and isocyanate with each other effectively. Besides, especially all CNTs caused to bubble on the inner surface of the PU foams could lead the decrease of sound absorption efficiency. The addition of 0.7 wt% CNTs leads to a significant increase of sound transmission loss at 30-40 Hz. At low percentage of CNT; 0.35 wt% and 0.7 wt%, the samples have better sound absorption compared with pure PU sample up to 100 Hz. Increasing the CNT will prevent the effective interaction between the polyol and the iscocyanate and hence have a bad sound absorption.

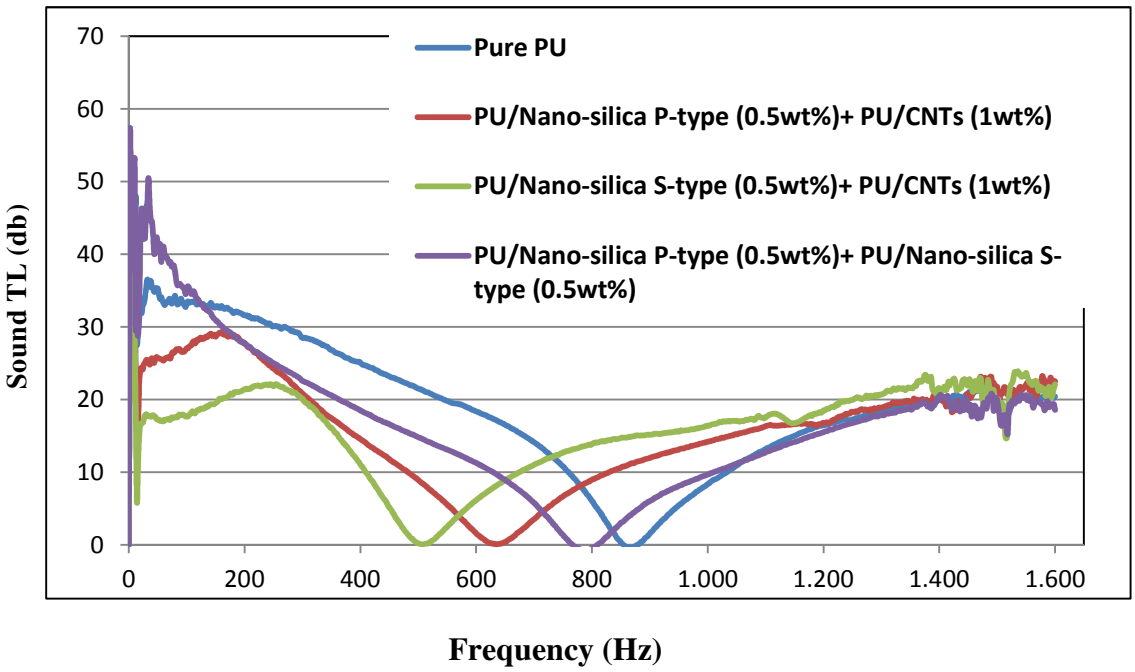


Fig. 4.5 : Sound tranmission loss of PU/ nano-silica/ CNTs added PU foam.

Now referring to the fig. 4.5, it was observed that at the mid frequency level, the pure PU has better sound insulation properties. On the contrary, between 800-1000 Hz the Pure PU foam has the worst sound insulation properties. At the lower frequency level (0-200) it was observed that 0.5 wt% Nano-silica S-type and P-type has better sound absorption ratio.

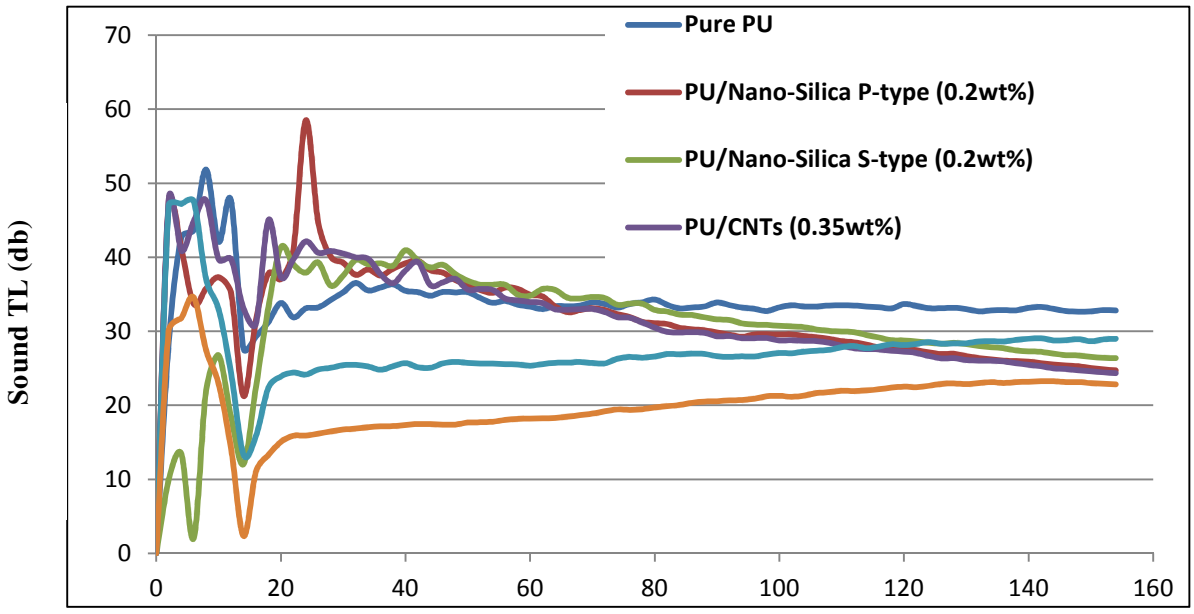


Fig. 4.6 : Sound Tranmission Loss of PU/ nano-silica/ CNTs added PU Foam.

Referring to the fig. 4.6, including 0.2 wt% of nano-silica P-type leads to a significant improvement at the 22-32 Hz. between 40 to 150 Hz, sound absorption characteristics of 0.2 wt% Nano-silica S-type, P-type and 0.35 wt% CNTs have substantially same acoustic properties. From 0 Hz to 20 Hz, 0.2 wt% Nano-silica P-type has much more better sound absorption ratio than Nano-silica S-type.

4.1.1 Sound Transmission Loss Measurements up to 6400 Hz

The acoustics group uses a two- microphone Bruel & Kjaer 4206 impedance tube to measure the sound transmission loss. In addition, an extension with two additional microphones is used to determine the transmission loss as well as the characteristic impedance and wave number within a material. The system consists of a 100 mm tube for a freqeuncy range of 100 – 1600 H and a 29 mm tube for frequencies of 100 - 6400 Hz. For measurement up to 6400 Hz, we used hand press for shaping the samples. As mentioned before we produced SiO2 nano particle added PU foam. P-type (porous type) SiO2 having 10 µm diameter can be called as “small silica” and s-type (spherical type) having 15-20 µm diameter can be called as “big silica” as a result of comparing with each other.

Table 4.1 : Percentage of the additives of the PU foam samples mixture for Measurement up to 6400 Hz

	CNTs	Nano-Silica S-Type	Nano-Silica P-Type
CNTs	0.35, 0.7 wt %		
Nano-Silica S-Type		0.2 wt %	
Nano-Silica P-Type			0.2, 0.5, 1 wt %

As shown in figure 4.7, silicon oxide nanoparticles, (P-type), having 10 µm diameter added to the PU foam was measured by using the impdance tube.

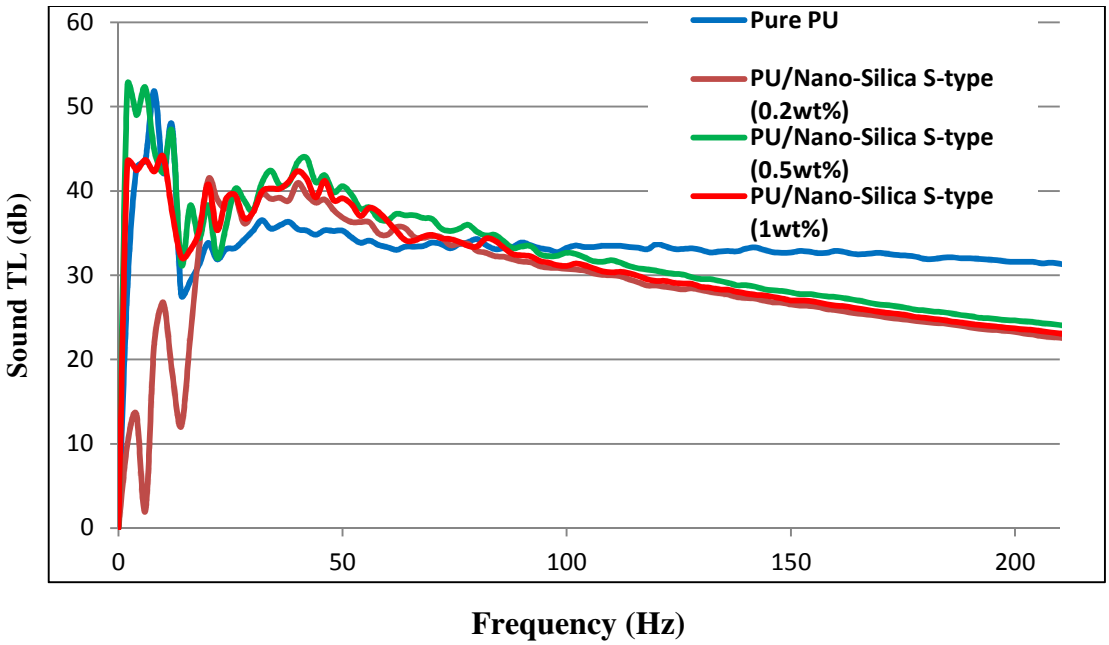


Fig. 4.7 : Sound Tranmission Loss of the P-Type SiO2 added PU Foam.

Referring to the fig 4.7, surprisingly, 0.2 wt% of silicon oxide nanoparticles (P-type) content have a better sound insulation comparing the pure PU foam, 0.5 wt% and 1 wt% of silicon oxide nanoparticles up to 5700 Hz. It can be seen that increasing the amount of the SiO2 content does not increase the sound insulation properties properly. In addition, 1 wt% of P-type SiO2 content overall has a poor effect comparing the 0.5 wt% of P-type SiO2. This graph has the same correlation such as CNTs added PU foam; it was observed that increasing the amount of CNTs prevents the interaction of polyol and isocyanate with each other effectively.

PU foam with CNTs added samples also shaped and dimensioned the for 6400 Hz measurement, such as cutting it to be form having a diameter 29 mm. Figure 4.8 shows the result of 0.35 wt% and 07 wt% CNTs added PU foam STL measurement.

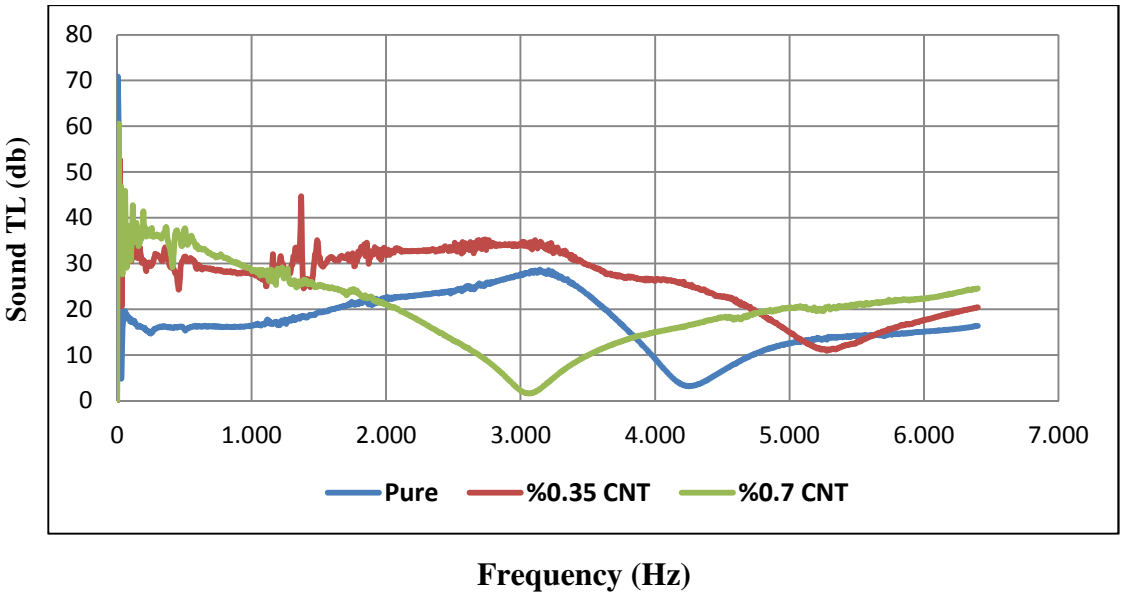


Fig. 4.8 : Sound Tranmission Loss Measurement of the CNTs added PU Foam up to 6400 Hz.

Referring to the figure 4.8, in a large-scale comparison 0.35 wt% of CNTs content have a better sound insulation comparing the pure PU foam and 0.7 wt% of CNTs. As mentioned before, it is seen again increasing the amount of CNTs has relatively better effect that Pure and 0.7 wt% of CNTs. Surprisingly, between 4800-6400 Hz, 0.7 wt% of CNTs has a better sound absorption.

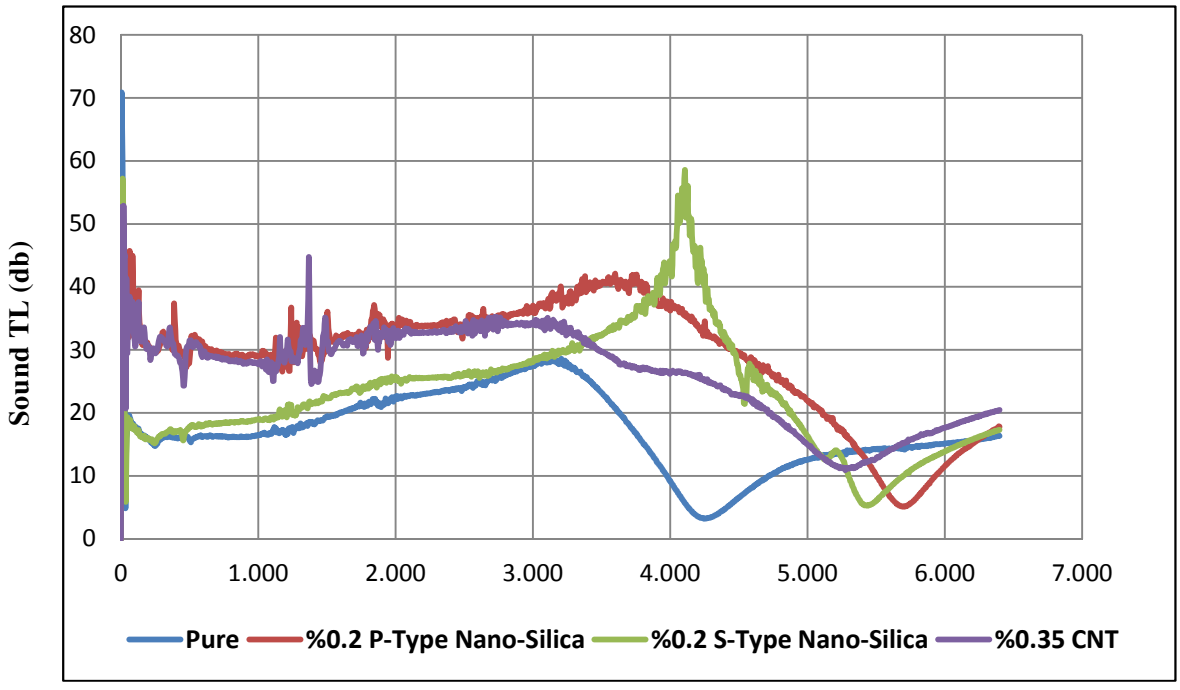


Fig. 4.9 : Sound Tranmission Loss Measurement of the PU/SiO2 (S-type, P-type),PU/CNTs added PU Foam up to 6400 Hz.

Figure 4.9 shows the STL of PU/nano-silica and CTNs foams with different content. One of the most surprising result is that 0.2 wt% small silica (P-type SiO2) has better sound absorption ratio overall than 0.2 wt% big silica (S-type SiO2). 0.2 wt% big silica (S-type SiO2) has a peak point about 4000-4200 Hz. Such outcome can be due to resonance effect at this frequency level. Almost every frequency level, pure PU foam has the worst sound transmission loss value. In fact, similar observations were mentioned at the previous graphs.

4.2 Sound Absorption Coefficients Measurements

As mentioned before, the PU foams may comprise various additive components for improving their acoustic performance. At this second step of the experimental part, PU/nano-silica and PU/CNTs nancomposite foams were again prepared and the effect of nano-silica and carbon nanotubes on their sound absorption ratio was investigated. It is well know that sound transmission loss (STL) and sound absorption coefficient are mostly used to determine the acoustical performance of the materials.

At this second part of experiments, more than 10 samples were produced; we especially wanted to observed that how was the acoustic effect of the CNTs addition to the PU. New samples with having 0, 0.1, 0.2, 0.35, 0.7 and 1 wt% CNTs were produced.

4.2.1 Preperation of PU Foams For Sound Abs. Coefficients Measurements

The polyols, surfactant, catalyst, and deionized water were weighed according to the foam formulation. First, polyol were gradually weighed, carbon nanotubes were added, and then mixed and stirred uniformly using a mechanically driven mixer at a rotational velocity of 1200 rpm for 20 s. Finally, isocyanate was added, and the mixture was stirred using a mechanically driven mixer for an additional 7 to 8 s.

Table 4.2 : Percentage of the additives of the PU foam samples mixture.

	CNTs	Nano-Silica S-Type	Nano-Silica P-Type
CNTs	0.1, 0.2, 0.35, 0.7, 1 wt %	0.2 wt% CNTs + 0.5 wt% S-Type	0.2 wt% CNTs + 1 wt% P-Type
Nano-Silica S-Type	0.2 wt% CNTs + 0.2 wt% S-Type		0.2 wt% P-Type + 0.2 wt% S-Type
Nano-Silica P-Type			

The mixture was poured into a rectangular mold with a dimension of 150 × 150 × 60 mm3. After curing for 2 hours, the foam was removed and aged for 24 h at room temperature. Here you can see the results of acoustic measurements.

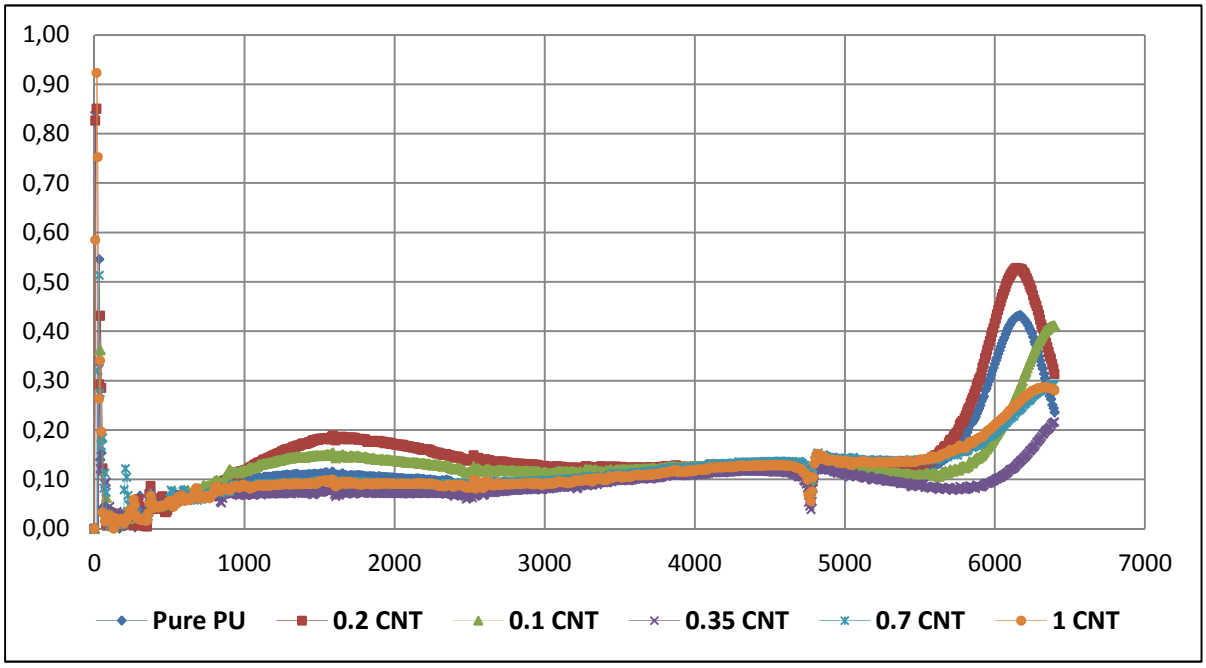


Fig. 4.10 : Sound absorption coefficient of the PU foam having different percent by weight of carbon nanotubes (Pure, %0.2, %0.1, %0.35, %0.7, %1).

Figure 4.10 shows the absorption coefficients of several CNTs added samples. It can be seen above that 0.2 wt% of CNTs has better effect than the rest of the samples. It is obivous that between 1000-4000 Hz and 5500-6400 Hz the 0.2 wt% of CNTs added PU foam shows better effect on sound tranmission loss. Adding 0.1 wt% of carbon nanotubes has relatively better effect than that of the 1 wt% which leads to a significant increase in absorption ratio at around 4800 Hz.

In broad frequency range from 100 to 5000 Hz, the sound absorption coefficients are generally above 0.1, with the maximum of 0.2. It can be seen that there is a significant increase at 6000 Hz where the sound ound absorption coefficients are maximum 0.5. It reveals that PU foam enclosing carbon nanotubes have good sound absorption ability in almost every frequency range.

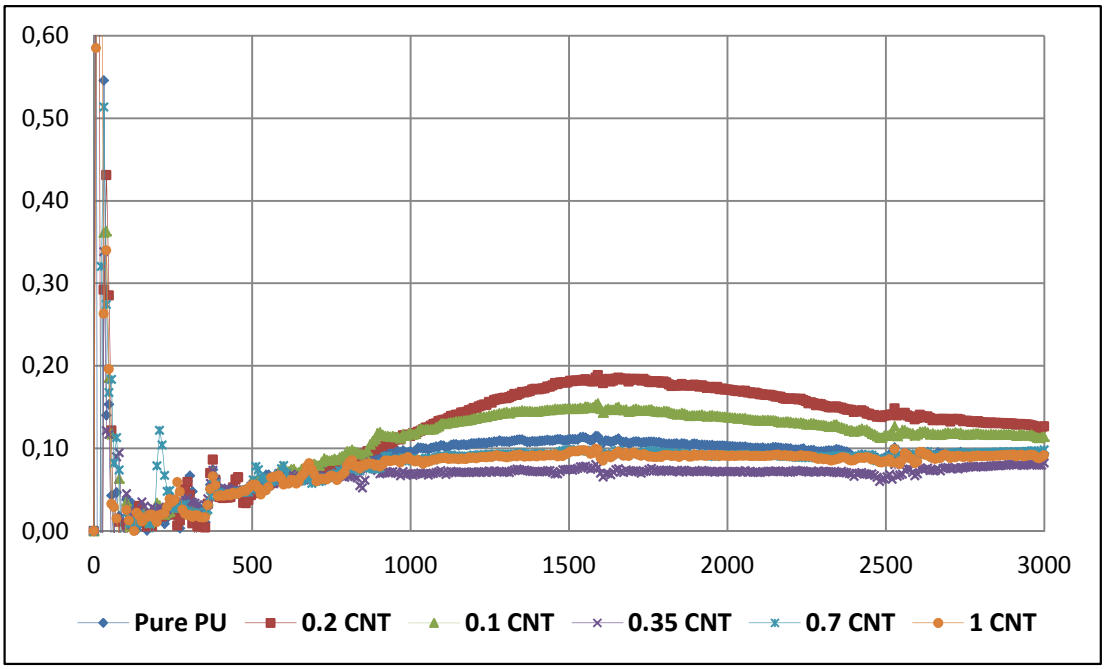


Fig. 4.11 : Sound absorption coefficient of the PU foam up to 3000 Hz having different percent weight of carbon nanotubes (Pure, %0.2, %0.1, %0.35, %0.7, %1).

As shown in figure 4.11, the absorption coefficients of several CNTs added samples up to 3000 Hz. It is clear that 0.2 wt% of carbon nanotubes added PU foam has the acoustic properties.

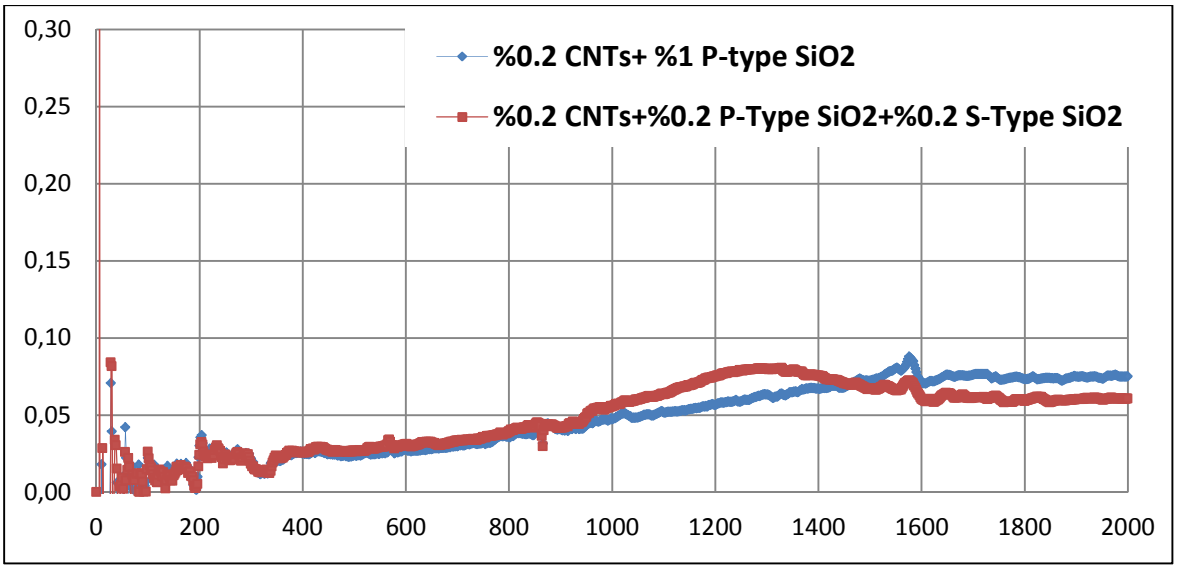


Fig. 4.12 : Sound absorption coefficient of the PU foam up to 2000 Hz.

Effects of combination of different additivies were also investigated. 0.2 wt% CNTs and 1 wt% P-type SiO2 were added to the PU foam and sound absorption coefficient were measured. In addition to this, 0.2 wt% CNTs, 0.2 wt% P-type (porous) SiO2 and 0.2 wt% S-Type (spherical) added to the PU Foam for the measurement of the sound absorption coefficient, respectively. Fig. 4.12 shows that presence of CNTs, S and P-type SiO2 content within foam structure can result in considerable enhancement in the sound absorption coefficient up to 1400 Hz.

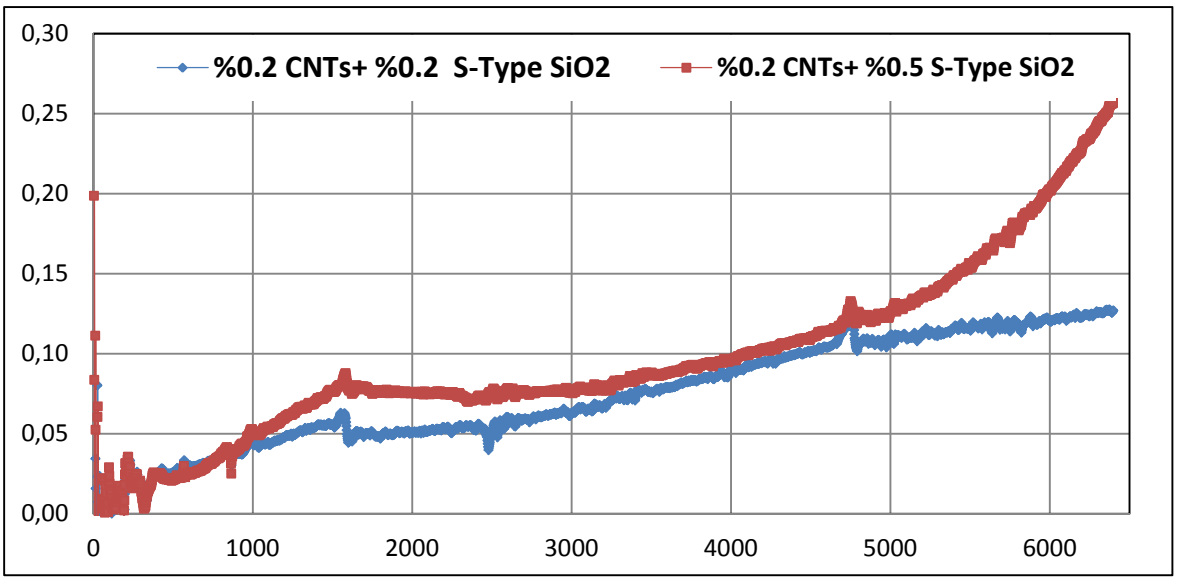


Fig. 4.13 : Sound absorption coefficient of the PU foam up to 6400 Hz.

Referring to the figure 4.13, the experimental results indicated that at low frequencies up to 1000 Hz, the SAC (sound absoption coefficient) value was about 0.05 for the both samples. Between 1000-6400 Hz, 0.2 wt% CNTs + 0.5 wt% S-Type SiO2 added PU foam has better SAC value than 0.2 wt% CNTs + 0.2 wt% S-Type SiO2 added PU foam. The content of the CNTs in the whole compound was kept at a constant value of 0.2% of the total weight; but depending on the sequence of mixing of constituent, added percent of S-type nano-silica was increased. It seemed that sound absorption coefficients were higher with the increasing the amount of the S-Type (spherical) SiO2 nanoparticles The 0.2 wt% CNTs + 0.5 wt% S-Type SiO2 added PU foam show a clear absorption peak over the range of 5000–6000 Hz, where human sensitivity to noise is very high. It is clear that at higher frequencies, the absorption coefficient consistently increases. This behaviour is characteristic of open-cell foams.

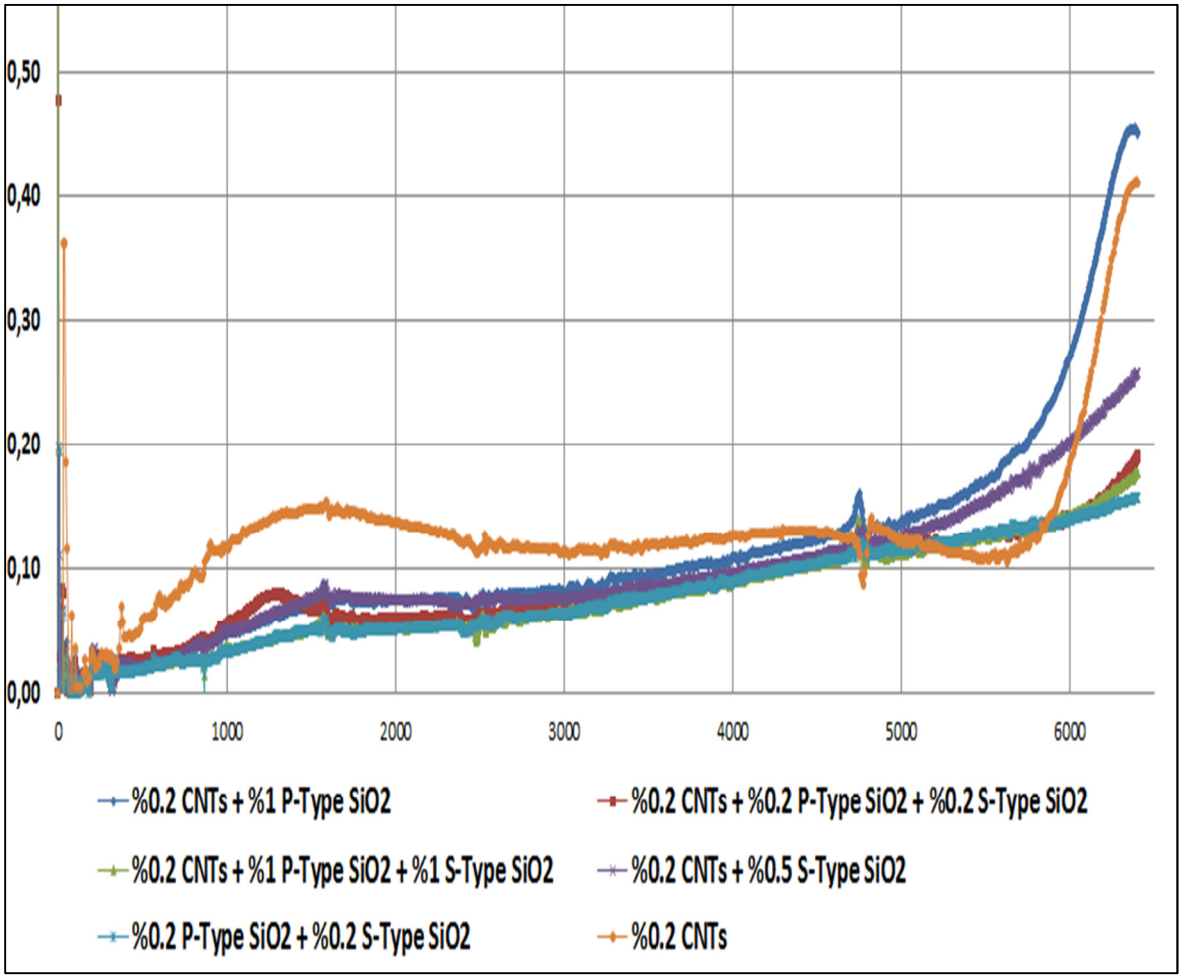


Fig. 4.14 : Sound absorption coefficient of the PU foam up to 6400 Hz.

6 samples having different contents also compared with each other. Referring to the fig. 5.5, the graph results indicated that at low frequencies up to 1000 Hz, [0.2 wt% CNTs + 0.2 wt% S-Type (spherical) SiO2 + 0.2 wt% P-Type (porous)] SiO2 added PU foam has better SAC value than the others. It is same with previous graphs that at higher frequencies, the absorption coefficient consistently increases. At mid and high-frequencies, especially between 2500-6400 Hz, [0.2 wt% CNTs + 1 wt% P-Type (porous)] PU Foam shows better acoustic properties, and the samples show a clear absorption peak over the range of 4700-4800 Hz. Surprisingly, around 600 Hz, [0.2 wt% CNTs + 1 wt% P-Type (porous)] PU foam has a great SAC value.

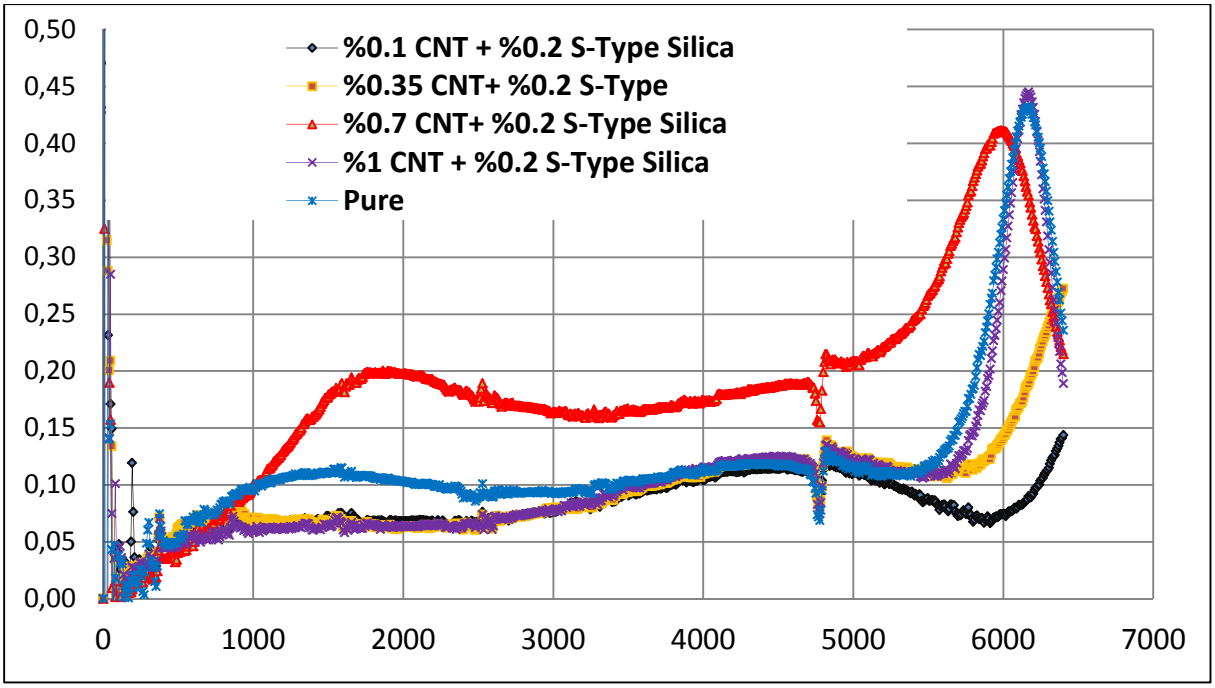


Fig. 4.15 : Sound absorption coefficient of the PU foam up to 6400 Hz.

0.2 wt% S-type nano-silica was constant in every 4 samples and four different samples having in different weight ratio of CNTs were tested. One of the most surprising result is that 0.7 wt% CNTs + 0.2 wt% S-type SiO2 added PU foam has better sound absorption ratio overall all frequencies levels. Almost every frequency level, pure PU foam has the worst sound transmission loss value. In fact, similar observations were mentioned at the

previous graphs. Up to 5800 Hz, rest of the samples have substantially same acoustic properties.

4.3 Future Works

Further studies are in progress to determine optimum combinations of CNTs and Nano-silica addition of the foam for best sound absorption coefficient in the low frequency. An effect of the fillers on mechanical and thermal properties of PU foam will also be investigated. In addition to this SEM observations will be used further analyses.

5. DISCUSSIONS

In this thesis, effects of the addition small amount of CNTs, Nano-Silica and their combinations into polyurethane foam on the sound absorption were investigated. The experimental results of this thesis showed that the sound absorption ability of polyurethane foam can be enhanced by modifying it with low loading of nano-silica and carbon nanotubes fillers. More than 40 samples at the different weight ratios of CNTs and Nano-Silica were developed and tested to determine their sound absorption properties. The tests showed that addition of 0.2 wt. % nano-silica in powder form and 0.35 wt. % carbon nanotube to polyurethane composition improved sound transmissions loss than that of pure polyurethane foam sample. Considering all of sound transmission loss test samples, 0.35 wt. % CNTs content has a better sound insulation comparing the other PU foams. Surprisingly, addition of 1 or 2 wt% CNTs has a poor effect than the pure PU foam. One the reason is that, increasing the amount of CNTs cause the prevent interaction of polyol and isocyanate with each other effectively. On the other hand, addition of 0.2 wt. % of Nano-Silica P-type leads to a significant improvement and P-type nano-silica has much better sound absorption ratio than nano-silica S-type substantially all along the frequency ranges. Increase in cell size may be attributed to increased gas diffusion. One hypothesis is that diffusion is enhanced at the polymer/filler interface due to poor interaction and increased free volume in the polymer [30]. With increasing density of the foams, their cell size decreases, and the sound absorption ratio of foams increases. This confirms that foams with small cell size absorb sound better than the foams with large cell size. The sound waves lead to the vibration of the thin cell walls and air inside cells. The sound energy is dissipated through vibration damping of the cell walls and air. Better sound absorption ability of foams with small cell size could be due to the high cell density resulting in more dissipation through vibration damping of the cell walls and air. the accumulation of excess CNT and nano-silica aggregate in void space of a cell can act as a barrier to influence the movement of the sound wave inside a cell. It should be stressed that the presence and distribution of nano-particles has a huge role to play in the nanocomposite especially at the higher particle

loading. More than 40 samples were produced and addition to the sound tranmsission loss, their sound absorption coefficient measuement also were measured. Adding of small amount mixture of CNTs and Nano-silica particles also investigaed. One of the most surprising result is that 0.7 wt% CNTs + 0.2 wt% S-type SiO2 added PU foam has better sound absorption ratio overall all frequencies levels. In broad frequency range from 100 to 5000 Hz, the sound absorption coefficients of CNTs added PU foams are generally above 0.1, with the maximum of 0.2. It was revealed that there was a significant increase at 6000 Hz where the sound absorption coefficients are maximum 0.5.

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